

Access DB# 83745

SEARCH REQUEST FORM

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Requester's Full Name: Andrew W. Wernicke Examiner #: 78959 Date: 1/7/03
 Art Unit: 1742 Phone Number 305 2167 Serial Number: 09/913938
 Mail Box and Bldg/Room Location: CVI 7012 Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: Copper Recovery Process

Inventors (please provide full names): Robert Pachalik, Egoner Lidner

Earliest Priority Filing Date: 2.11.1999

**For Sequence Searches Only* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.*

Please search attached claims copper recovery from
etch bath

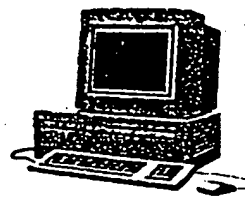
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	Type of Search	Vendors and cost where applicable
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Date Completed: <u>1/5/03</u>	Litigation _____	Lexis/Nexis _____
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Online Time: <u>40</u>	Other _____	Other (specify) _____

EIC1700

Search Results

Feedback Form (Optional)



Scientific & Technical Information Center

The search results generated for your recent request are attached. If you have any questions or comments (compliments or complaints) about the scope or the results of the search, please contact *the EIC searcher* who conducted the search *or contact*:

Kathleen Fuller, Team Leader, 308-4290, CP3/4 3D62

Voluntary Results Feedback Form

➤ I am an examiner in Workgroup:

Example:

1713

➤ Relevant prior art found, search results used as follows:

- ☐ 102 rejection
- ☐ 103 rejection
- ☐ Cited as being of interest.
- ☐ Helped examiner better understand the invention.
- ☐ Helped examiner better understand the state of the art in their technology.

Types of relevant prior art found:

- ☐ Foreign Patent(s)
- ☐ Non-Patent Literature
(journal articles, conference proceedings, new product announcements etc.)

➤ Relevant prior art not found:

- ☐ Results verified the lack of relevant prior art (helped determine patentability).
- ☐ Search results were not useful in determining patentability or understanding the invention.

Other Comments:

Drop off completed forms in CP3/4 - 3D62 .

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FILE COVERS 1907 - 7 Jan 2003 VOL 138 ISS 2

FILE LAST UPDATED: 6 Jan 2003 (20030106/ED)

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L8 5 SEA FILE=HCAPLUS ABB=ON L7 AND (PLAT? OR ELECTROPLAT?)
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KATHLEEN FULLER EIC 1700/PARKER LAW 308-4290

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 PROCESSING COMPLETED FOR L19
L20 57 DUP REM L11 L15 L16 L17 L18 L19 (7 DUPLICATES REMOVED)

=> D L20 ALL 1-57

L20 ANSWER 1 OF 57 HCAPLUS COPYRIGHT 2003 ACS DUPLICATE 1
 AN 2002:865370 HCAPLUS
 TI New method for the purification and recycling of spent solutions of hexavalent chromium
 AU Benaben, Patrick
 CS Surface Treatment Dep., Ecole Nationale Superieure des Mines, St. Etienne, Fr.
 SO Galvanotecnica e Nuove Finiture (2002), 12(4), 204-208
 CODEN: GNFIF9
 PB Associazione Italiana Finiture dei Metalli
 DT Journal
 LA Italian
 CC 56 (Nonferrous Metals and Alloys)
 AB **Purifn.** of hexavalent chromium solns. used in chromium **plating** industry, or as **etching** solns. for plastics surfaces or **copper** foils, becomes more and more of major interest due to economical, tech. and environmental reasons. A new entirely chem. method useful to **purify** and recycle hexavalent chromium solns. (**etching** and **electroplating** solns.) developed at the Ecole Nationale Superieure des Mines de Saint-Etienne (France) and patented, is described. This method allows **extn.** of all metallic contaminating cations by pptn. and filtration, while anions remains in the soln.: this process allows to recycle sulfate anion and/or any other anion (used as catalyst). The major effect of depolluting chromic acid solns. is energy saving in the case of **electroplating** and keeping an efficient **etching** power for chromic acid soln. The paper discuss process costs and the economical advantages of the method, which consents an overall saving of about 20% with ref. to the replacement of the soln. with a new and fresh one. The project is sponsored by an AESF Research Grant for one year.

RE.CNT 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Anon; Hard Chromium Plating: Techniques, Markets and alternative Process - Proceedings- 1st International Colloquium 1995, P135
- (2) Anon; Hard and Decorative Chromium Plating: New Trends and New Applications - Proceedings - 2nd International Colloquium 1998, P131
- (3) Benaben, P; FR 2669323 HCAPLUS

- (4) Benaben, P; Galvano-Organo 1998, 686, PR471
(5) Mandich, N; Plating and Surface Finishing 1997, V84(12), P82 HCAPLUS
(6) Mortier, F; CETIM Informations 51, P27
(7) Newby, K; Hard and Decorative Chromium Plating: New Trends and New Applications - Proceedings 2nd International Colloquium 1998, P95
(8) Pajunen, P; Hard Chromium Plating: Techniques, Markets and alternative Process - Conference Acts 1995, P178
(9) Parker, J; Bulletin du Cercle d'Etudes des Metaux (to be published in March 2002 issue) 2001, VXXVII(4), PXXXII

L20 ANSWER 2 OF 57 METADEX COPYRIGHT 2003 CSA

AN 2002(7):43-377 METADEX

TI Recovery of nitric acid and valuable metals from spent nitric etching solutions of printed circuit board.

AU Ahn, J.-W. (Daejin University); Ahn, J.-G. (Korea Institute of Geoscience and Mineral Resources); Lee, M.-S. (Mokpo National University)

SO Journal of the Korean Institute of Metals and Materials (Jan. 2002) 40, (1), 116-121, Graphs, 5 ref.
ISSN: 0253-3847

DT Journal

CY Korea, Republic of

LA Korean

AB A study has been made on the recovery of nitric acid and valuable metals such as Cu, Sn and Pb from the spent nitric etching solutions. The nitric acid was extracted effectively by TBP but the heavy metals such as Fe, Cu, Sn and Pb were not extracted by TBP from the spent nitric etching solutions. From the experimental results, 95% of nitric acid in spent etching solution was extracted at O:A ratio of 3:1 in five stages by 60% TBP, and 98% of nitric acid was stripped from the loaded organic phase at O:A ratio of 1:1 in four stages by distilled water. After extraction of nitric acid, Cu was effectively recovered as a metal by electrowinning and Sn was successfully removed by precipitation methode as the form of hydroxide or hydrated oxide by adjusting pH of the raffinate solution. Finally, Pb was recovered by cementation with iron scrap at above 65 deg C. Parameters controlling the cementation process, such as temperature, pH and the effect of the additives were investigated.

CC 43 Refining and Purification

CT Journal Article; Iron: Recovering; Copper: Recovering; Tin: Recovering; Lead (metal): Recovering; Etchants: Recycling; Industrial wastes: Recycling; Electrowinning; Precipitation; Electronic devices: Fabrication

ET Cu; Sn; Pb; Fe; O

L20 ANSWER 3 OF 57 HCAPLUS COPYRIGHT 2003 ACS DUPLICATE 2

AN 2002:917113 HCAPLUS

TI Electrochemical **recovery** process of spent **Cu etching solution**

AU Lee, Chang-Hyun; Wyi, Jung-Il; Moon, Jae-Yeol; Jang, Si-Sung; Lee, Chung-Bae; Han, Sung-Ho; Hwang, Woon-Suk

CS Division of Materials Science and Engineering, Inha Univ., S. Korea

SO Han'guk Pusik Hakhoechi (2001), 30(2), 104-109
CODEN: HPHADI; ISSN: 0253-312X

PB Corrosion Science Society of Korea

DT Journal

LA Korean

CC 72 (Electrochemistry)

AB Wastewaters from the metal **plating**, finishing and **extg** . industries contain many metallic ions which are very harm to human body and environmentally hazardous. Therefore. many researches have been performed to develop economical and effective wastewater treatment systems. The **recovery** of metallic ions from industrial

wastewaters using an electrochem. method had an advantage over other methods with respect to the pollution prevention and recycling of valuable metals. In this process, the **recovery of copper** from PCB wastewaters was investigated using the electrochem. method. At first, the electrochem. behavior of the wastewater was evaluated by cathodic polarization characteristics with pH and initial **copper** concn. in the spent **Cu etching soln.** And it was concluded that the redn. process of **copper** was accomplished by two steps from **Cu(II)** via **Cu(I)** From the **recovery** expts. at various conditions which did not occur the chloride gas evolution, the highest **recovery** efficiency was obtained in the c.d. of 3.5A/dm², the pH of 1.85 and the initial **copper** concn. of 32,000ppm.

L20 ANSWER 4 OF 57 HCAPLUS COPYRIGHT 2003 ACS

DUPLICATE, 3

AN 2000:531856 HCAPLUS

DN 133:107786

TI **Copper recovery from an alkaline etching solution**

IN Pacholik, Robert; Lidmer, Gunnar

PA Mecer Holdings Corp, Swed.

SO Swed., 23 pp.

CODEN: SSXXAY

DT Patent

LA Swedish

IC ICM C23F001-46

ICS C23F017-00; C25F007-02; H05K003-00

CC 54-2 (Extractive Metallurgy)

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	SE 512160	C2	20000207	SE 1999-748	19990302
	WO 2000052229	A1	20000908	WO 2000-SE66	20000114
	W:		AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, VZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM		
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	EP 1165861	A1	20020102	EP 2000-902242	20000114
	R:		AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, RO		
PRAI	SE 1999-748	A	19990302		
	WO 2000-SE66	W	20000114		
AB	An alk. etching soln. (e.g., an ammoniacal etching soln.) and rinsing water from electroplating of patterns with Cu are extd. with an org. soln. contg. a reagent forming a complex compd. with Cu . The alk. bath is recycled to etching . The Cu -contg. org. soln. is contacted with an aq. O-contg. soln. (e.g., a (S + O)-contg. soln.). Cu is passed from the org. soln. to the aq. soln., and the org. soln. is recycled. The Cu is recovered from the aq. soln. by electrolysis. Flow of the aq. soln. to the electrolytic cell is partially diverted to control the Cu content in the soln.				
ST	copper recovery spent etching soln				
IT	Etching				

(copper recovery from spent alk. etching soln.)

IT Process control
(for copper recovery from spent alk. etching soln.)

IT Recycling
(in copper recovery from spent alk. etching soln.)

IT 7440-50-8P, Copper, preparation
RL: PUR (Purification or recovery); PREP (Preparation)
(recovery from spent alk. etching soln.)

L20 ANSWER 5 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 2001-009334 [02] WPIX

DNN N2001-007022 DNC C2001-002491

TI Copper removal system comprises an electrolytic cell having anode and cathode separated by a copper ion-permeable membrane.

DC E13 J01 L03 M25 X25

IN GOOSEY, M; GOOSEY, M T

PA (SHIL) SHIPLEY CO; (SHIL) SHIPLEY CO LLC

CYC 29

PI EP 1043408 A2 20001011 (200102)* EN 7p C22B015-14
R: AL AT BE CH CY DE DK ES FI FR GB GR IE IT LI LT LU LV MC MK NL PT
RO SE SI

JP 2000317458 A 20001121 (200108) 6p C02F001-469

CN 1278564 A 20010103 (200124) C23F001-46 <--

KR 2001020719 A 20010315 (200159) C22B003-00

US 6391188 B1 20020521 (200239) C02F001-461

ADT EP 1043408 A2 EP 2000-650027 20000406; JP 2000317458 A JP 2000-106399
20000407; CN 1278564 A CN 2000-117945 20000407; KR 2001020719 A KR
2000-18095 20000407; US 6391188 B1 US 2000-545154 20000407

PRAI GB 1999-7848 19990407

IC ICM C02F001-461; C02F001-469; C22B003-00; C22B015-14; C23F001-46
ICS B01D061-44; C02F001-46; C02F001-62; C25B009-00; C25B015-00;
C25C001-12

AB EP 1043408 A UPAB: 20010110
NOVELTY - A copper removal system (10) comprises an electrolytic cell having anode (16) and cathode (14) separated by a copper ion-permeable membrane (18).
DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for a process for removing copper from a mixture containing copper complexing agent comprising providing the specified system; and adding to the system a fluid containing copper and copper complexing agent; and electrolytically treating the fluid.
USE - The system is used for recovery and removal of copper from solutions such as spent etchant -type solutions produced from manufacturing printed circuit board for electrical applications. It is also applied in other manufacturing processes.
ADVANTAGE - The system provides solutions having less than 10000 ppm of copper, preferably less than 1000, 100, or 10 ppm.
DESCRIPTION OF DRAWING(S) - The figure schematically shows a copper removal system.
Copper removal system 10
Cathode 14
Anode 16
Membrane 18
Anolyte 20
Catholyte 22

Dwg.1/1
FS CPI EPI
FA AB; GI; DCN
MC CPI: E06-D08; E11-Q02; E35-A; J01-C03; J01-D05; L03-H04E; M25-E01
EPI: X25-R01C

L20 ANSWER 6 OF 57 HCAPLUS COPYRIGHT 2003 ACS
AN 2002:681425 HCAPLUS
DN 137:357451
TI Purification and recycling process of hexavalent chromium solutions using
a low cost chemical method
AU Benaben, Patrick; Popakul, Joseph
CS SMS Division, Ecole Nationale Supérieure des Mines, Saint-Etienne,
F-42023, Fr.
SO Proceedings - AESF SUR/FIN Annual International Technical Conference
(2000) 776-783
CODEN: PASCFU
PB American Electroplaters and Surface Finishers Society
DT Journal; (computer optical disk)
LA English
CC 60-2 (Waste Treatment and Disposal)
Section cross-reference(s): 56, 72
AB A new chem. method used to **purify** and to recycle hexavalent
chromium **solns.** (**electroplating** and **etching**
solns.) is described. This method allows the **extn.** of
metallic cations (99% of iron, **copper** cations are removed) after
pptn. and filtration. The pollution/depollution efficiency can be
controlled by cond. measurements. The major effect of de-polluting
chromic acid soln. is to minimize the energy consumption in the case of
electroplating and to keep the efficiency of the **etching**
power of chromic acid **soln.** An approach of process costs shows
the economical interest of this method: the total cost of the
purified chromic acid is less (about 20%) than the cost of chromic
acid replacing when the soln. is polluted.
ST chromium **electroplating etching solns** purifn
recycling
IT Etching
(electrochem.; purifn. and recycling process of hexavalent chromium
solns. for)
IT Silicates, processes
RL: CPS (Chemical process); PEP (Physical, engineering or chemical
process); REM (Removal or disposal); PROC (Process)
(fluoro-; purifn. and recycling process of hexavalent chromium solns.
contg.)
IT Purification
Recycling
(of hexavalent chromium solns. using low cost chem. method)
IT Hydroxides (inorganic)
RL: CPS (Chemical process); PEP (Physical, engineering or chemical
process); PNU (Preparation, unclassified); REM (Removal or disposal); PREP
(Preparation); PROC (Process)
(pptn. of metal hydroxides in purifn. and recycling process of
hexavalent chromium solns.)
IT Organic compounds, uses
RL: NUU (Other use, unclassified); USES (Uses)
(purifn. and recycling process of hexavalent chromium solns. contg.)
IT Electrodeposition
(purifn. and recycling process of hexavalent chromium solns. for)
IT Filtration
Precipitation (chemical)

- (purifn. and recycling process of hexavalent chromium solns. using)
- IT 1333-82-0P, Chromium trioxide
RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)
- (purifn. and recycling process of hexavalent chromium solns. cong.)
- IT 14808-79-8, Sulfate, uses
RL: NUU (Other use, unclassified); USES (Uses)
- (purifn. and recycling process of hexavalent chromium solns. contg.)
- IT 7429-90-5, Aluminum, processes 7439-89-6, Iron, processes 7439-92-1, Lead, processes 7440-02-0, Nickel, processes 7440-31-5, Tin, processes 7440-50-8, Copper, processes 7440-66-6, Zinc, processes
RL: REM (Removal or disposal); PROC (Process)
- (purifn. and recycling process of hexavalent chromium solns. contg.)
- IT 11104-59-9, Chromate
RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
- (purifn. and recycling process of hexavalent chromium solns. using low cost chem. method)

RE.CNT 8 THERE ARE 8 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

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- (2) Benaben, P; Galvano-Organo 1998, 686, P471 HCAPLUS
- (3) Ecole des Mines; Hard Chromium Plating: Techniques, Markets and alternative Process - Conference Acts 1995, P135
- (4) Ecole des Mines; Hard and Decorative Chromium Plating: New Trends and New Applications - Proceedings 2nd Colloquium 1998, P131
- (5) Mandich, N; Plating and Surface Finishing 1997, V84(12), P82 HCAPLUS
- (6) Mortier, F; CETIM Informations 51, P27
- (7) Newby, K; Hard and Decorative Chromium Plating: New Trends and New Applications - Proceedings 2nd International Colloquium 1998, P95
- (8) Pajunen, P; Hard Chromium Plating: Techniques, Markets and alternative Process - Conference Acts 1995, P178

L20 ANSWER 7 OF 57 METADEX COPYRIGHT 2003 CSA

AN 2001(5):43-208 METADEX

TI Research and development of processes for treatment of waste waters and spent technological solutions with the purpose of purification from As, Ga, In and Sb compounds by using the copper etching spent solutions.

AU Meshalkin, A.V. (Moscow Institute of Steels and Alloys)

SO Tsvetnaya Metallurgiya (Nov.-Dec. 2000) 11-12, 54

ISSN: 0132-0785

DT Journal

CY Russian Federation

LA Russian

AB The conditions and processes for purification of waste waters of the gallium arsenide and copper sulfuric acid etching with utilization of spent Fe-containing solutions are studied. The kinetic regularities of copper cementation on steel chip are revealed in the process of decontamination of the spent Cu-containing solutions of iron chloride. The iron (II) chloride solutions prepared are utilized in the process of decontamination of the spent etching reagents of GaAs by coprecipitation.

CC 43 Refining and Purification

CT Journal Article; Gallium: Extraction; Indium: Extraction; Antimony: Extraction; Copper: Extraction; Effluents: Refining; Precipitation: Composition effects; Iron compounds; Etchants; Spent liquors: Reactions (chemical); Reaction kinetics; Steels; Chips; Cementation; Water purification

ET " As; Ga; In; Sb; Fe; Cu; As*Ga; As sy 2; sy 2; Ga sy 2; GaAs; Ga cp; cp; As
cp

L20 ANSWER 8 OF 57 JICST-EPlus COPYRIGHT 2003 JST

AN 1000598339 JICST-EPlus

TI Copper Recycling Technology from Alkaline Etchant.

AU FUJITA Y; WATANABE H

CS Meltex Inc.

SO Fain Puretingu (Fine Plating), (2000) no. 58, pp. 23-26. Journal Code:
L1753A (Fig. 2, Tbl. 6, Ref. 2)
ISSN: 1342-2901

CY Japan

DT Conference; Article

LA English

STA New

CC SC05060V; NC03030V (628.477; 621.382.002.2)

CT printed board; **etching solution**; dissolution;

copper; **recovery** of useful material; solvent

extraction; **copper** oxide; **copper** sulfate;

chloride; ammonium compound; **copper** compound; electrolysis;

boiling(phase transition); recycle; resource recycling; **copper**

complex; purity; secondary metal; waste water treatment

BT substrate(plate); plate classified by application; plate(material);

electric apparatus and parts; parts; 1B group element; transition metal;

metallic element; element; fourth row element; resource recovery;

recovery; **extraction**; separation; metal oxide; oxide;

chalcogenide; oxygen group element compound; oxygen compound; 1B group

element compound; transition metal compound; sulfate(salt); sulfur oxoate;

sulfur compound; oxoate; chlorine compound; halogen compound; halide;

onium compound; hydrogen compound; nitrogen compound; nitrogen group

element compound; electrochemical reaction; chemical reaction; phase

transition; reuse; utilization; regeneration; 1B group element

complex; transition metal **complex**; metal **complex**

; **complex**(compound); coordination compound; compound(chemical);

degree; virgin metal; sewage treatment; water and sewage treatment;

treatment

L20 ANSWER 9 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1999-602297 [52] WPIX

DNN N1999-444082 DNC C1999-175403

TI Liquid-liquid **extraction** process especially for regenerating
ammoniacal **etching solutions** used in circuit board
manufacture.

DC D15 J01 L03 M14 V04

IN CELI, A M; CELI, I L

PA (CELI-I) CELI I L

CYC 86

PI DE 19815288 A1 19991007 (199952)* 6p C23F001-46 <--

WO 9951795 A1 19991014 (199952) DE C23F001-46 <--

RW: AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU MC MW NL

OA PT SD SE SL SZ UG ZW

W: AE AL AM AT AU AZ BA BB BG BR BY CA CH CN CU CZ DE DK EE ES FI GB

GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU

LV MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR

TT UA UG US UZ VN YU ZA ZW

AU 9937053 A 19991025 (200011) C23F001-46 <--

DE 19980595 T 20001026 (200055) C23F001-46 <--

ADT DE 19815288 A1 DE 1998-19815288 19980406; WO 9951795 A1 WO 1999-EP2299

19990403; AU 9937053 A AU 1999-37053 19990403; DE 19980595 T DE

1999-19980595 19990403, WO 1999-EP2299 19990403

FDT" AU 9937053 A Based on WO 9951795; DE 19980595 T Based on WO 9951795

PRAI DE 1998-19815288 19980406

IC ICM **C23F001-46**

ICS B01D011-04; C02F001-26; C23G001-36

AB DE 19815288 A UPAB: 19991210

NOVELTY - A liquid/liquid **extraction** process for alkaline **etching solution** regeneration comprises coalescence phase separation, washing and stripping alkali from the washing liquid.

DETAILED DESCRIPTION - A process for regenerating an alkaline metal-containing **etching solution** by liquid/liquid **extraction** to remove metal ions comprises coalescence separation of the heavy phase (**etching solution**) and the light phase (organic solution), washing of the **extraction** phase, **recovery** of the alkali and the metal components and removal of the alkali from the washing liquid by stripping.

An INDEPENDENT CLAIM is also included for a countercurrent apparatus for carrying out the above process, comprising a coalescence separation device for the light and heavy phases in each **extraction** and washing stage, a hydraulic stirrer, a washing or countercurrent washing stage for the **extraction** and back **extraction** phases, equipment for **recovering** the alkali and metal components from the **extraction** phase and a stripper for alkali removal from the washing liquid.

USE - For regenerating alkaline **etching solutions**, especially ammoniacal **etching solutions** used in the manufacture of circuit boards having **copper** circuit lines protected against etching by metals such as Sn, Sn/Pb, Ni/Sn or Au.

ADVANTAGE - The process is energy saving, waste water-free, inexpensive and nonpolluting.

DESCRIPTION OF DRAWING(S) - The drawing shows an apparatus for carrying out the process of the invention.

Vacuum stripper As

Coalescence separation device KKA

Electrolyte bath El

Sulfate precipitation bath Se

Dwg.1/1

FS CPI EPI

FA AB; GI

MC CPI: D04-B07; J01-C; L03-H04E9; M14-A03

EPI: V04-R15A

L20 ANSWER 10 OF 57 HCAPLUS COPYRIGHT 2003 ACS

AN 1999:408332 HCAPLUS

DN 131:106171

TI Using water-soluble polymers to remove dissolved metal ions

AU Thompson, Julia A.; Jarvinen, Gordon

CS PolyIonix Separation Technologies, Inc., USA

SO Filtration & Separation (1999), 36(5), 28-32

CODEN: FSEPAA; ISSN: 0015-1882

PB Elsevier Science Ltd.

DT Journal

LA English

CC 60-2 (Waste Treatment and Disposal)

Section cross-reference(s): 8, 71, 72

AB Polymer Filtration (PF), a metal ion **recovery** technol. that uses metal binding polymers to clear up process streams, has been used to treat a variety of aq. streams, including rinse water from acid zinc **plating** baths, rinse water from ammoniacal **etch soln.**, and processing water contaminated with plutonium-238. During the treatment of the acid zinc rinse soln., the zinc metal ions

were **recovered** with a high degree of efficiency (>99.3%), the **recovered** metal ion soln. was shown to be reusable in the **plating** bath, and the effluent was reused as rinse water. **Complexed** metal ions are often difficult to remove from soln. by pptn., however, PF is often very efficient in removing metal ions from these solns. because the proprietary polymers successfully compete with the mol. **complexing** agents for the metal ions. In the case of ammonia-**complexed copper** ions in the **etch** rinse soln., PF exhibited a high **copper** removal rate efficiency (>98%). In the case of removal of plutonium from processing water, the combination of the specially prepd. water-sol. polymers with ultrafiltration greatly enhanced the efficiency of the plutonium removal compared to the use of tradition pptn. technol.

- ST **electroplating** zinc removal polymer chelation; etching copper removal polymer chelation; plutonium removal radioactive wastewater polymer chelation; polymer chelation metal wastewater rinse water treatment
- IT Wastewater treatment
(**complexation**; using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT Etching
(electrochem.; using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT Wastes
Wastes
(electrodeposition; using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT Wastewater treatment
(ultrafiltration; using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT Radioactive wastewater
(using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT Electrodeposition
Electrodeposition
(wastes; using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT Polymers, reactions
RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent); USES (Uses)
(water-sol. metal chelators; using water-sol. polymers to remove dissolved metal ions from acid zinc **plating bath** and ammoniacal **etch soln.** rinse waters and plutonium-238-contaminated processing water)
- IT 7440-50-8, Copper, processes 7440-66-6, Zinc, processes 13981-16-3, Plutonium-238, processes
RL: PEP (Physical, engineering or chemical process); POL (Pollutant); REM

(Removal or disposal); OCCU (Occurrence); PROC (Process)
(using water-sol. polymers to remove dissolved metal ions from acid
zinc **plating bath** and ammoniacal **etch**
soln. rinse waters and plutonium-238-contaminated processing
water)

RE.CNT 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE

- (1) Bayer, E; Isr J Chem 1985, V26, P40 HCAPLUS
- (2) Cheryan, M; Ultrafiltration and Microfiltration Handbook 1998, P302
- (3) Geckeler, K; Environ Sci & Techn 1996, V30, P725 HCAPLUS
- (4) Geckeler, K; Environ Sci Tech 1996, V30, P725 HCAPLUS
- (5) Novikov, A; Radiochim Acta 1989, V46, P35 HCAPLUS
- (6) Smith, B; ACS Symposium Series 1999, 716, P294
- (7) Smith, B; J Radioanalytical Nucl Chem 1998, V234, P219 HCAPLUS
- (8) Smith, B; Proc of the National Surface Finishers Meeting 1995
- (9) Smith, B; US 5643456 Process for the displacement of cyanide ions from
metal-cyanide complexes 1997 HCAPLUS
- (10) Smith, B; US 5766478 Water-soluble polymers for recovery of metal ions
from aqueous streams 1998 HCAPLUS
- (11) Thompson, J; Proceedings of the 20th AESF/EPA Conference for Environmental
Excellence 1999, P277 HCAPLUS

L20 ANSWER 11 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1998-234889 [21] WPIX

CR 1998-141281 [13]; 1998-141419 [13]

DNC C1998-073602

TI Treatment of aq. soln. of ferric ion-contg. iron chloride - includes
pouring powdered iron having ionisation tendency higher than that of the
impurity metals into aq. soln. of reduced iron chloride, and separating
impurity metal ions.

DC D15 E31 L03 M14 M24 M28 P53

IN INOSHITA, T; KITAZAWA, T; MATSUMOTO, H; MITO, K; NAGAOKA, Y; NAGASHIMA, M;
YOSHINO, H

PA (ASTE-N) ASTEC IRII KK; (ASTE-N) ASTEC IRIE CO LTD

CYC 4

PI JP 10072691 A 19980317 (199821)* 10p C25C001-06

KR 98001838 A 19980330 (199902) C01G049-00

US 5954854 A 19990921 (199945) C22B003-46

TW 416995 A 20010101 (200134) C23F001-46 <--

ADT JP 10072691 A JP 1996-265378 19960913; KR 98001838 A KR 1997-28263
19970627; US 5954854 A US 1997-883630 19970626; TW 416995 A TW 1997-109005
19970627

PRAI JP 1996-188506 19960628; JP 1996-188508 19960628; JP 1996-194005
19960703

IC ICM C01G049-00; C22B003-46; **C23F001-46**; C25C001-06

ICS C01G049-10; C02F001-461

AB JP 10072691 A UPAB: 20010620

The treatment comprises:

(a) reducing ferric ions in an aq. soln. of iron chloride contg.
impurity metal ions, including **copper** and nickel, to a ferrous
ions, to obtain an aq. soln. of reduced iron chloride;

(b) pouring powdered iron having ionisation tendency higher than that
of the impurity metals into the aq. soln. of reduced iron chloride, and
separating the impurity metal ions to obtain a aq. soln. of refined iron
chloride; and

(c) oxidizing the ferrous ions in the aq. soln. of the refined iron
chloride to form the ferric ions.

The reduction process comprises:

(i) supplying the aq. soln. of iron chloride to an electrolytic bath;

(ii) reducing the ferric ion in the aq. soln. of iron chloride to the

ferrous ion on a negative plate:

(iii) trapping a chlorine gas evolved from a positive plate; and

(iv) **extracting** the aq. soln. of reduced iron chloride from the electrolytic bath.

USE - The method removes the impurity metal ions from an **etching** waste liq. (the aq. soln. of iron chloride) evolved in etching a lead frame for integrated circuit, or large scale integrated circuit, or a television shadow mask, and **recovers** the concn. of the ferrous ion to the predetermined level to regenerate the etching waste liquid.

ADVANTAGE - Reducing the ferric ion in the aq. soln. of iron chloride to the ferrous ion by a cathode reaction reduces the ferric ion without increasing the total concn. of the iron ion in the soln. The method eliminates the need for increasing the amt. of the aq. soln. of iron chloride by using a dilution soln. to lead the concn. of the ferric ion to the predetermined concn. in regenerating the aq. soln. of iron chloride and retains the original amt. of the soln. The result reduces costs for treating the excess soln. and offers a compact treatment facilities. The amt. of powdered iron for regenerating the aq. soln. of iron chloride is reduced to reduce treatment costs.

Dwg.0/6

FS CPI GMPI

FA AB; DCN

MC CPI: D04-A01M; D04-A01P; D04-B05; E11-N; E11-Q02; E35-U04; L03-H04E3;
L04-C07C; L04-C23; M14-A03; M28-A

L20 ANSWER 12 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1998(10):57-1426 METADEX

TI The use of mixed extractants in a unique membrane SX system for the recovery of copper from acid cupric chloride solutions.

AU Ernt, W.D.; Dimmit, J.

SO Minerals, Metals and Materials Society/AIME. 420 Commonwealth Dr., P.O. Box 430, Warrendale, PA 15086, USA. 1998. 317-343, Graphs, 19 ref. Conference: EPD Congress 1998, San Antonio, TX, USA, 16-19 Feb. 1998 ISBN: 0-87339-388-0

DT Conference Article

CY United States

LA English

AB A membrane based mixed extractant process was developed for selective removal of copper from waste acidic cupric chloride etchant solutions found in printed wire board manufacturing. The process uses a mixture of Adogen 381 (tri-isooctylamine), MOC-45 (ketoxime) and MOC-55TD (aldoxime) in a kerosene diluent. The mixed extractants recover the copper from a hydrochloric acid medium and transfers it to a sulfuric acid medium. The process also utilizes unique wetted membranes to separate the aqueous and organic phases. The driving force for these membranes is not pressure but the difference in surface tension between the two phases. By using these membranes, complete phase separation results. There is no physical entrainment contamination as found in conventional systems. The only cross contamination is the solubility concentration of one phase in the other. This however is less than 10 mg/l.

CC 57 Finishing

CT Conference Paper; Copper: Recovering; Etchants; Liquid membrane extraction; Recycling; Extractors: Materials selection

L20 ANSWER 13 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1999(4):43-150 METADEX

TI Recovery of copper from spent etching solution by extraction.

AU Huang, Sh. (Academia Sinica); Ling, Y. (Academia Sinica)

SO Huagong Yejin (Engineering Chemistry and Metallurgy) (Aug. 1998) 19, (3),

271-273, Graphs, 5 ref.
ISSN: 1001-2052

DT Journal
CY China
LA Chinese

AB LIX-54 was chosen as extraction reagent to treat the spent etching solution for copper recovery. The extraction conditions were investigated. For an etching solution containing Cu 107.39 g/L, NH3 128.4 g/L, after the processing of 3-stage extraction, the copper content can be reduced to about 30 g/L without ammonia extracted, and the raffinate can be favorably recycled to the etching solution. No apparent degradation of the extractant was observed.

CC 43 Refining and Purification
CT Journal Article; Copper: Recovering; Etching; Degradation
ET Cu; H*N; NH3; N cp; cp; H cp

L20 ANSWER 14 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1998(5):42-287 METADEX

TI Recovering of valuable metals from waste etching solution by using fine iron dust.

AU Nagashima, M. (Asutech)

SO Kogyo Zairyo (Engineering Materials) (1997) 45, (7), 60-64,
Photomicrographs
ISSN: 0452-2834

DT Journal
CY Japan
LA Japanese

AB The recovering of valuable metals (copper, nickel, etc.) from waste etching solutions in IC industry and electronic component industry by iron powder reducing agent is studied. The characteristics of Fe powders are described. The quality control specifications of reproduced etching solution are tabulated. The extraction technology of Ni in flow stirring bath is discussed. The properties of recovered Cu and Ni are examined.

CC 42 Extraction and Smelting
CT Journal Article; Copper: Recovering; Nickel: Recovering; Iron: End uses; Metal powders: End uses; Reducing agents: Materials selection; Quality control; Specifications; Extraction; Stirring; Baths; Etching
ET Fe; Ni; Cu

L20 ANSWER 15 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1997-043699 [05] WPIX

DNN N1997-036209 DNC C1997-014061

TI Treating **etching soln.** used in printing circuit board
mfr. - includes contacting ammoniacal soln. with **extraction**
agent non-miscible with water, washing resulting agent contg. valuable metal content several times.

DC L03 M14 V04

IN KEHL, R; SCHWAB, W
PA (HENK) HENKEL KGAA

CYC 29

PI	DE 19521352	A1 19961219 (199705)*	9p	C23F001-46	<--
	WO 9641902	A1 19961227 (199706)	DE 28p	C23F001-46	<--
	RW: AT BE CH DE DK ES FI FR GB GR IE IT LU MC NL PT SE				
	W: AU BR CA CN CZ HU JP KR MX RU US				
	AU 9660044	A 19970109 (199717)		C23F001-46	<--
	EP 833961	A1 19980408 (199818)	DE	C23F001-46	<--
	R: BE DE FR GB IT NL				
	AU 692108	B 19980528 (199833)		C23F001-46	<--
	KR 98702743	A 19980805 (199932)		C22B003-00	
	JP 11507700	W 19990706 (199937)	20p	C23F001-46	<--

EP 833961 B1 19990915 (199942) DE C23F001-46 <--
 R: BE DE FR GB IT NL
 DE 59603091 G 19991021 (199950) C23F001-46 <--
 MX 9710101 A1 19980301 (200002) C23F001-46 <--
 US 6045763 A 20000404 (200024) B01D011-00
 TW 388774 A 20000501 (200062) C23F001-18 <--
 MX 200742 B 20010131 (200222) C23F001-46 <--

ADT DE 19521352 A1 DE 1995-19521352 19950612; WO 9641902 A1 WO 1996-EP2385
 19960603; AU 9660044 A AU 1996-60044 19960603; EP 833961 A1 EP 1996-917489
 19960603, WO 1996-EP2385 19960603; AU 692108 B AU 1996-60044 19960603; KR
 98702743 A WO 1996-EP2385 19960603, KR 1997-706150 19970903; JP 11507700 W
 WO 1996-EP2385 19960603, JP 1997-502564 19960603; EP 833961 B1 EP
 1996-917489 19960603, WO 1996-EP2385 19960603; DE 59603091 G DE
 1996-503091 19960603, EP 1996-917489 19960603, WO 1996-EP2385 19960603; MX
 9710101 A1 MX 1997-10101 19971211; US 6045763 A WO 1996-EP2385 19960603,
 US 1997-983064 19971212; TW 388774 A TW 1996-102937 19960311; MX 200742 B
 MX 1997-10101 19971211

FDT AU 9660044 A Based on WO 9641902; EP 833961 A1 Based on WO 9641902; AU
 692108 B Previous Publ. AU 9660044, Based on WO 9641902; KR 98702743 A
 Based on WO 9641902; JP 11507700 W Based on WO 9641902; EP 833961 B1 Based
 on WO 9641902; DE 59603091 G Based on EP 833961, Based on WO 9641902; US
 6045763 A Based on WO 9641902

PRAI DE 1995-19521352 19950612

REP 1.Jnl.Ref; DE 4334696; EP 5415; US 3743585; US 3981968; US 4012482; US
 4083758; US 4222832

IC ICM B01D011-00; C22B003-00; C23F001-18; C23F001-46
 ICS C22B003-26; C22B007-00; C22B015-00; C23F001-00

AB DE 19521352 A UPAB: 19970129
 The ammoniacal solution used in etching printed
 circuit boards is treated by contacting with an extraction agent
 non-miscible with water. The agent now contg. the valuable metal content
 (mainly Cu) is then washed in several steps with an aq. liq.
 before being subjected to one or more stripping stages in which the metal
 is transferred to an aq. phase. In the first washing stage, water is used
 with a pH of below 6.5. Before being reused this wash water is contacted
 with the extraction agent.
 USE - Used for treating ammoniacal etching solns.
 used in the prodn. of printed circuit boards.
 ADVANTAGE - The washing process ensures that most ammonia is
 recovered from the extraction agent and is not lost. It
 can be recycled to the etching solution.
 Dwg.1/1

FS CPI EPI
 FA AB; GI
 MC CPI: L03-H04E2; M14-A03
 EPI: V04-R15A

L20 ANSWER 16 OF 57 METADEX COPYRIGHT 2003 CSA
 AN 1997(11):43-354 METADEX
 TI Application of solvent extraction to the treatment of industrial wastes.
 AU Shibata, J. (Kansai University); Yamamoto, H. (Kansai University);
 Matsumoto, S. (Kansai University)
 SO Minerals, Metals and Materials Society/AIME. 420 Commonwealth Dr., P.O.
 Box 430, Warrendale, PA 15086, USA. 1996. 481-487, 8 ref.
 Conference: Second International Symposium on Extraction and Processing
 for the Treatment and Minimization of Wastes 1996, Scottsdale, Arizona,
 USA, 27-30 Oct. 1996
 ISBN: 0-87339-369-4
 DT Conference Article
 CY United States

LA English

AB It is important to recover and reuse the metal values contained in various industrial wastes in a viewpoint of environmental preservation. Most of industrial products are made through the processes to separate impurities in raw materials, solid and liquid wastes being necessarily discharged as industrial wastes. Chemical methods such as solvent extraction, ion exchange and membrane, and physical methods such as heavy media separation, magnetic separation and electrostatic separation are considered as the methods for separation and recovery of the metal values from the wastes. In this paper, some examples and recovery of the metal values from the wastes. In this paper, some examples of the application of solvent extraction to the treatment of wastes are introduced. The treatment of solid wastes such as Ni-Co alloy scrap, Sm-Co alloy scrap, fly ash and flue dust, and liquid wastes such as plating solution, the rinse water, etching solution and pickling solution are accomplished using solvent extraction technique.

CC 43 Refining and Purification

CT Conference Paper; Iron: Recovering; Nickel: Recovering; Cobalt: Recovering; Samarium: Recovering; Vanadium: Recovering; Zinc: Recovering; Copper: Recovering; Recycling; Metal scrap; Solvent extraction; Waste disposal; Industrial wastes

ET Co*Ni; Co sy 2; sy 2; Ni sy 2; Ni-Co; Co*Sm; Sm sy 2; Sm-Co

L20 ANSWER 17 OF 57 HCAPLUS COPYRIGHT 2003 ACS DUPLICATE 4

AN 1996:578581 HCAPLUS

DN 125:226958

TI Flowsheets development for recovery of nonferrous metal values from secondary resources by solvent **extraction**

AU Mukherjee, T. K.; Gupta, C. K.

CS Materials Group, Bhabha Atomic Research Centre, Bombay, 400085, India

SO Emerging Separation Technologies for Metals II, Proceedings of a Symposium, Kona, Hawaii, June 16-21, 1996 (1996), 249-262. Editor(s): Bautista, Renato G. Publisher: Minerals, Metals & Materials Society, Warrendale, Pa.

CODEN: 63IMA3

DT Conference; General Review

LA English

CC 54-0 (Extractive Metallurgy)

AB A review with 17 refs. Typical examples of secondary resources in the Indian scenario, mention can be made of spent catalysts, metal/alloy scrap, ash, consumed batteries, flue dust, slag, sludge and slime, pickling solns., spent acids, **plating rinse solns.**, spent **etchants**, waste water from synthetic fiber manuf. and from tanneries etc. These wastes constitute a source of a variety of non ferrous metals. In the processing of secondary resources like these, the techniques of hydrometallurgy such as solvent **extn.** play a pivotal role. This paper outlines the efforts made to use solvent **extn.** to **recover** (1) base metals such as **copper**, zinc, nickel and cobalt from a no. of secondary resources like cake, and sludge (2) refractory metals like molybdenum and vanadium from sulfide byproducts and spent catalyst and (3) nuclear metal like uranium from phosphoric acid. In the case of base metals, process flowsheet involving the use of acidic **extractants** such as DEHPA and PC88A have been optimized. The problem of iron removal from the leach liquor, which influences the metal **recovery** process significantly, has drawn a special emphasis. In the case of refractory metals, basic **extractants** like Alamine 336 has been pressed into service to produce kg quantities of pure salts of molybdenum and vanadium. Finally, the paper gives a brief account of plant experience in **recovering** uranium from phosphoric acid, using a solvent system composed of DEHPA and

TOPO.

ST review nonferrous metal recycling waste

IT **Extraction**

Recycling

Waste solids

(flowsheets development for recovery of nonferrous metal values from secondary resources by solvent **extn.**)

IT Metals, preparation

RL: PUR (Purification or recovery); PREP (Preparation)

(nonferrous, flowsheets development for recovery of nonferrous metal values from secondary resources by solvent **extn.**)

L20 ANSWER 18 OF 57 WPIX (C) 2003 THOMSON DERWENT DUPLICATE 5

AN 1995-076361 [11] WPIX

DNN N1995-060620 DNC C1995-033966

TI Multi-step recovery of spent metal **etching solns.** -
involving **extracting** metal ions using oxime cpds. as ion
exchanger.

DC J01 L03 M14 V04

IN CELI, A M

PA (INTE-N) IN.TEC ITAL INT ENVIRONMENT TECHNOLOGY; (ECOS-N) ECOSCIENT SA

CYC 7

PI EP 638662 A1 19950215 (199511)* EN 15p C23F001-46 <--

R: BE DE ES FR GB

US 5520814 A 19960528 (199627) 10p C02F001-26

IT 1261515 B 19960523 (199704) B01J000-00

EP 638662 B1 19980701 (199830) EN C23F001-46 <--

R: BE DE ES FR GB

DE 69411333 E 19980806 (199837) C23F001-46 <--

ES 2123744 T3 19990116 (199909) C23F001-46 <--

ADT EP 638662 A1 EP 1994-830399 19940810; US 5520814 A Cont of US 1994-290497
19940815, US 1995-521280 19950830; IT 1261515 B IT 1993-RM558 19930813; EP
638662 B1 EP 1994-830399 19940810; DE 69411333 E DE 1994-611333 19940810,
EP 1994-830399 19940810; ES 2123744 T3 EP 1994-830399 19940810

FDT DE 69411333 E Based on EP 638662; ES 2123744 T3 Based on EP 638662

PRAI IT 1993-RM558 19930813

REP 2.Jnl.Ref; EP 5413; JP 55091979; JP 55148177; US 3440036; US 4083758

IC ICM B01J000-00; C02F001-26; **C23F001-46**

ICS C02F001-28

AB EP 638662 A UPAB: 19950322

Spent metal **etching solns.** are recovered by: a)**extracting** the metal ions by ion exchange, b) washing the liq. ion
exchanger with water, c) vaporising the wash water, d) crystallising the
concentrate, e) filtering the regenerated **etching soln**., f) restoring the quality of the soln., g) **extracting** the
metal from the metal-loaded ion exchanger, h) washing the liq. ion
exchanger, i) neutralising the wash water, j) filtering, and k) recovering
the metal electrolytically.ADVANTAGE - The metal content of the spent soln. e.g. from circuit
board prodn., is virtually entirely recovered, in an economic and
environmentally sound manner.

Dwg.0/7

FS CPI EPI

FA AB; GI

MC CPI: J01-A01; J01-B; J01-D04; J01-F02; J03-B; L04-C07C; M14-A02

EPI: V04-R15

L20 ANSWER 19 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1995-148126 [20] WPIX

DNN N1995-116337 DNC C1995-068689

TI " Ammoniacal copper-contg. **etching soln.** regeneration -
using hydroxy-phenon-oxime-contg. **extractant** for copper
extn.

DC E14 J01 L03 M14 V04

IN BUHR, H; HUELSCHER, M; REINHOLD, V

PA (VULK-N) VULKAN ENG GMBH

CYC 1

PI DE 4334696 A1 19950413 (199520)* 7p C23F001-46 <--

ADT DE 4334696 A1 DE 1993-4334696 19931012

PRAI DE 1993-4334696 19931012

IC ICM **C23F001-46**

ICS C25C001-12

AB DE 4334696 A UPAB: 19950530

In the regeneration of ammoniacal **copper-contg. etching soln.** by solvent **extn.** (4) to give a **copper** -depleted **etching soln.** (50) and a loaded **extractant** (52) which is stripped with an aq. soln. (54) for selective ammonia removal and then with a sulphuric acid soln. for **copper** removal before return to the **extn.** unit (4), the novelty is that (a) the **copper** content of the **etching soln.** (50) is reduced to a value approaching 0 g/l by solvent exten. using a hydroxyphenonoxime-contg. **extractant** (52); and (b) the aq. soln. (54) of the ammonia stripping stage is recirculated.

Pref. the **extractant** (52) is 2-hydroxy-5-nonylacetophenonoxime.

USE - For regenerating spent **etching soln.** from e.g. **etching** of electronic circuit boards.

ADVANTAGE - The **extractant** has very high affinity for **copper** so that an almost completely de-coppered **etching soln.** is **recovered**. Recirculation of the aq. soln. avoids the need for continuous fresh soln. (wash water) supply or soln. disposal so that costs are reduced. Only small amounts of by-products, requiring special disposal, are produced.

Dwg.1/1

FS CPI EPI

FA AB; GI; DCN

MC CPI: E10-A18B; E11-Q02; E35-A; J01-C01; L03-H04E2; M14-A02; M25-B04;
M25-E01; M25-G08

EPI: V04-R15A

L20 ANSWER 20 OF 57 JAPIO COPYRIGHT 2003 JPO

AN 1995-025613 JAPIO

TI PRODUCTION OF CUPROUS CHLORIDE

IN KANAYAMA NOBUO; AWAYA MASARU; SUZUKI MICHIMASA; HIRAHARA BUNJI

PA TSURUMI SODA CO LTD

PI JP 07025613 A 19950127 Heisei

AI JP 1993-194255 (JP05194255 Heisei) 19930708

PRAI JP 1993-194255 19930708

SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1995

IC ICM C01G003-05

AB PURPOSE: To efficiently and inexpensively produce highly pure cuprous chloride by adding a reducing agent to a cupric chloridecontaining solution high in the concentrations of **copper** and hydrochloric acid, filtering off impurities from the obtained chloro **complex** solution, and subsequently cooling the filtrate.
CONSTITUTION: For example, a cupric chloride **etching waste solution** is concentrated into a solution having a **copper** concentration of 11wt.% and above and a hydrochloric acid concentration of >=9wt.%. The cupric chloride-containing solution is mixed with a reducing agent such as iron or **copper** to reduce the cupric chloride into

- " cuprous chloride. The cuprous chloride forms a chloro **complex** and is dissolved to provide a chloro **complex** solution. Impurities are filtered off from the chloro **complex** solution. The chloro **complex** solution is cooled at e.g. approximately 20°C to deposit the cuprous chloride from the solution by the utilization of the difference between the solubilities due to the difference of temperatures, followed by filtering out the cuprous chloride, thus **recovering** the crystals of the highly pure cuprous chloride.

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L20 ANSWER 21 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1993-262097 [33] WPIX

DNN N1993-201311 DNC C1993-117030

TI Recovery of metal from metal halide soln. contg. **complex** of halogen and metal - by measuring concn. according to light transmittance and adding required amt. of reducing agent.

DC J01 M14 S03

PA (TSUM) TSURUMI SODA KK

CYC 1

PI JP 05179466 A 19930720 (199333)* 5p C23F001-46 <--

ADT JP 05179466 A JP 1991-359701 19911227

PRAI JP 1991-359701 19911227

IC ICM C23F001-46

ICS G01N021-59

ICA C02F001-70

AB JP 05179466 A UPAB: 19931119

Metal from metal halide soln. contg. **complex** halogen and metal by adding a reducing agent. Light having a specific wavelength penetrates through the metal halide soln. to determine the transmittance. The concn. of **complex** is determined from the transmittance. Reducing agent is added to the soln. at a rate corresp. to the concn. of **complex**. **Recovery** equipment has sampling means, the light irradiation means, means to determine transmittance, and the means to determine the concn. of **complex**.

USE/ADVANTAGE - The method is applied to **recover** Cu from cupric chloride **etching** soln. after **etching** of dry film. The concn. of metal halide is measured promptly and easily without using colouring agent.

Dwg. 1/3

FS CPI EPI

FA AB; GI

MC CPI: J01-F02D; M14-A02

EPI: S03-E04B1A

L20 ANSWER 22 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1993-262096 [33] WPIX

DNC C1993-117029

TI Removal of halogen from copper halide soln. - by contacting with anion exchange resin layer for selective absorption, eluting with solvent etc..

DC A91 J01 M14

PA (TSUM) TSURUMI SODA KK

CYC 1

PI JP 05179465 A 19930720 (199333)* 7p C23F001-46 <--

ADT JP 05179465 A JP 1991-359699 19911227

PRAI JP 1991-359699 19911227

IC ICM C23F001-46

ICS C01G003-04

AB JP 05179465 A UPAB: 19931119

Removal of halogen comprises: contacting the **copper** halide soln.

contg. free halogen, halogen, and **copper complex** with anion exchange resin layer; adsorbing the anion **complex** in the **copper** halide soln. to the anion exchange resin layer selectively against the free halogen; passing a solvent through the anion exchange resin layer to release the anion from the anion exchange resin layer in a form of cation and free halogen; **recovering** the solvent soln.

USE/ADVANTAGE - Used to remove Cl⁻ from cupric chloride

etching soln. after the **etching** of a dry film.

The total amount of halogen in the **copper** halide soln. is significantly reduced compared with the total amount of halogen including in the original **copper** halide soln., which in turn reduces the consumption of metal replacing the **copper**. **Copper** is efficiently **recovered**.

Dwg.0/5

FS CPI

FA AB

MC CPI: A12-W11E; J01-C; J01-D04; M14-A02

L20 ANSWER 23 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1993-089077 [11] WPIX

DNN N1993-067699 DNC C1993-039779

TI **Recovering** hydrochloric acid and **copper** sulphate from **copper** chloride waste soln. - by reacting sulphuric acid with waste **copper** chloride, then sepg. condensed soln. into hydrochloric acid and **copper** sulphate by crystallisation.

DC E36 L03 M14 V04

PA (ASAK-N) ASAKA RIKEN KOGYO KK

CYC 1

PI JP 05033168 A 19930209 (199311)* 7p C23F001-46 <--

JP 3085549 B2 20000911 (200046) 7p C23F001-46 <--

ADT JP 05033168 A JP 1991-159258 19910629; JP 3085549 B2 JP 1991-159258 19910629

FDT JP 3085549 B2 Previous Publ. JP 05033168

PRAI JP 1991-159258 19910629

IC ICM **C23F001-46**

ICS B01D009-02; C01B007-01; C01G003-10; C02F001-04; C23G001-36;

H05K003-06

AB JP 05033168 A UPAB: 19931122

Method comprises **recovering** HCl from condensed reaction soln.

obtd. by reacting H₂SO₄ with waste CuCl₂ soln. from

etching process and then sepg. the condensed soln. into HCl and CuSO₄ crystals through crystallisation process.

Pref. distn. step is added after **recovering** HCl and hydrochloric acid, to **recover** conc. hydrochloric acid. More specifically, H₂SO₄ is added to distn. bottom as entrainer to conduct **extractive** distn. to **recover** conc. HCl acid as effluent, while condensing the H₂SO₄ liq. to **recover** it as entrainer.

USE/ADVANTAGE - Used for **recovering** HCl and CuSO₄ from CuCl₂ waste soln. which is produced during **etching** of Cu PCBs.

Dwg.0/1

FS CPI EPI

FA AB; DCN

MC CPI: E11-Q01; E31-B03D; E35-A; L03-H04E2; L03-H04E9; M14-A02

EPI: V04-R15

L20 ANSWER 24 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1993-160214 [20] WPIX

DNN N1993-122940 DNC C1993-070749

TI Regeneration of sulphuric acid, per oxo di sulphate **etching**

solns. contg. copper - by using a process requiring no interruptions for accumulated copper removal.

DC J03 L03 M14 M28 V04 X25

IN HEINZE, G; THIELE, W; WILDNER, K

PA (EILE-N) EILENBURGER CHEM WERK GMBH

CYC 1

PI DE 4137022 A1 19930513 (199320)* 10p C23G001-36

DE 4137022 C2 19931125 (199347) 10p C23G001-36

ADT DE 4137022 A1 DE 1991-4137022 19911111; DE 4137022 C2 DE 1991-4137022 19911111

PRAI DE 1991-4137022 19911111

IC ICM C23G001-36

ICS C23F001-46; C25B001-28; C25B009-00; C25C001-12

AB DE 4137022 A UPAB: 19931113

The method for regeneration of sulphuric-acid, peroxodisulphate **etching solutions** containing **copper** consists of cathodic reduction and precipitation of the bulk of **copper** in a **copper recovery** cell, followed by **copper** precipitation and regeneration of the peroxodisulphate respectively in the cathode and anode spaces of a divided peroxodisulphate regeneration cell. The solution from the **copper recovery** cell has a residual **copper** content from 0.05 to 5 g/litre. With optimal adjustment of the regeneration cell, regeneration of the **etching solution** can be carried out with an energy consumption of 1/7 kWh per kg of sodium peroxodisulphate. The cell operates with bubble-driven catholyte circulation and continuous removal of precipitated residual **copper** by means of integrated solid/liquid separation stages.

USE/ADVANTAGE - The process can be used in manufacture of printed circuit boards. It is environment-friendly and does not have to be interrupted for removal of accumulated **copper**.

Dwg.1/3

FS. CPI EPI

FA AB; GI

MC CPI: J03-B; L03-H04E2; L03-H04E9; M14-A

EPI: V04-R15A; X25-R06

L20 ANSWER 25 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1993(10):43-345 METADEX

TI A New Extractant Mixture for Recovery of Copper From Hydrochloric Etching Solution.

AU Kyuchoukov, G. (Bulgarian Academy of Sciences); Mishonov I. (Bulgarian Academy of Sciences)

SO Solvent Extraction and Ion Exchange (Sept. 1993) 11, (4), 555-567, Graphs, 8 ref.

ISSN: 0736-0299

DT Journal

CY United States

LA English

AB Studies were performed with a mixture of commercial extractants (Alamine 336 + LIX 54) used for copper recovery from hydrochloric etching solutions to transfer Cu from hydrochloric to sulfuric medium. The most appropriate ratio between the components of the extractant mixture was found. The separate steps of the process (extraction, scrubbing, stripping and conditioning) were optimized.

CC 43 Refining and Purification

CT Journal Article; Copper: Recovering; Etchants: Recovering; Industrial wastes: Recovering; Recovering; Solvent extraction; Solvents

ET Cu

L20 ANSWER 26 OF 57 METADEX COPYRIGHT 2003 CSA

AN* 1993(3):42-246 METADEX

TI Recovery of Copper From alpha -Etchant Solution by Electrowinning and Cementation.

AU Won, C.W. (Chungnam National University); Kang, Y. (Chungnam National University); Chun, B.S. (Chungnam National University); Sohn, H.Y. (University of Utah)

SO Metallurgical Transactions B (Feb. 1993) 24B, (1), 192-197, Graphs, Photomicrographs, Diffraction patterns, 8 ref. ISSN: 0360-2141

DT Journal

CY United States

LA English

AB To recover Cu by electrowinning, an experimental apparatus was used. The reaction vessel was 2 L in volume and was agitated at 150 rpm. The cathode was a stainless steel plate of 2 x 10 cm size, the anode was a graphite rod, and the distance between the electrodes was 7 cm.

CC 42 Extraction and Smelting

CT Journal Article; Copper: Extraction; Electrowinning; Electrometallurgy; Cementation

ET Cu

L20 ANSWER 27 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1992-150907 [18] WPIX

DNN N1992-112702 DNC C1992-069935

TI Regenerating and **recovering** metals from chloride-contg. solns. - process is economical and capable of being automated, effective, partic for **copper**.

DC L03 M12 M14 M25 V04

IN ARTMANN, B; LIEBER, H W; MATSCHINER, H; REICHEL, K

PA (HOEL-N) HOELLMUELLER MASCHBAU GMBH H

CYC 15

PI WO 9206227 A 19920416 (199218)* DE

RW: AT BE CH DE DK ES FR GB GR IT LU NL SE

W: JP US

ADT WO 9206227 A WO 1991-EP1903 19911007

PRAI DE 1990-4031744 19901006

REP 1.Jnl.Ref; US 3877932; US 4422911

IC C22B015-00; **C23F001-46**; C23G001-36

AB WO 9206227 A UPAB: 19931006

Regenerating process and appts. for metal **recovery** from chloride solns. esp. from **etching**, pickling, and surface washing, and is advantageous for Cu and other metal ions. The metals for **recovery** are displaced from solns. by H at rates of 0.6-1.8 kg/m³ per hr. under pressure (up to 0.5 MPa) at 10-60 deg.C) in appts. which is equipped with a circulating and a thickening/filtration system.

USE/ADVANTAGE - Esp. suitable for **recovering Cu** effluents from acid washing printed circuit boards. The process is continuous, has low appts. and chemical input costs and is capable of automisation.

In an example, 15l of CuCl₂ soln. (6g/lCu) with pH and at 50 deg.C was fed into reaction container 1 and circulated by means of side channel pump 2 under pressure of H of 0.3 MPa the whole undergoing sepn. in solid sepn. container 4. After 10 mins. the Cu concn. had dropped to 0.02 g/l, and the **extract** in 4, Cu paste-142 g represented the **recovery** of 89.5 g of Cu. :

1/1 (0/11)

FS CPI EPI

P. CI

L03-H04E9; M25-E01; M25-G08

V04-R15B

ULLER EIC 1700/PARKER LAW 308-4290

- L20 ANSWER 28 OF 57 JAPIO COPYRIGHT 2003 JPO
 AN 1991-071696 JAPIO
 TI MANUFACTURE OF CIRCUIT BOARD WITH BUILT-IN RESISTOR
 IN HANAJIMA OSAMU; TOKI SOTARO; NOGUCHI MITSUHIKO
 PA TOPPAN PRINTING CO LTD
 PI JP 03071696 A 19910327 Heisei
 AI JP 1989-207260 (JP01207260 Heisei) 19890810
 PRAI JP 1989-207260 19890810
 SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1991
 IC ICM H05K003-06
 ICS H01C017-06; H05K001-16
 AB PURPOSE: To improve an **etching solution** exclusive to a high conductive material layer and a resistive material layer and its etching selectivity so as to obtain the resistive layer of required resistance and to improve a work environment in safety by using a specific **etching solution**.
 CONSTITUTION: A resistive material layer 2 of nickel alloy and a high conductor layer 1 are formed on, at least, one side of an insulating support 3. In etching, the same etching liquid is used in processes shown by figures b-d, an etching liquid of pH7.5-9.5 composed of ammonium sulfate. **copper** sulfate (valent **copper** ion concentration: 5-200g/l) and hydroxide is used in processes shown by figures f-g. The hydroxide concerned is sodium hydroxide, potassium hydroxide, or the like, and **copper** subsists partially as ammonium **complex** to show a **recovery** mechanism of the **etching solution**. By this setup, a circuit board with a built-in accurate resistor can be obtained without the corrosion of a resistive material layer, and a problem concerning as a work environment can be eliminated.
 COPYRIGHT: (C)1991,JPO&Japio
- L20 ANSWER 29 OF 57 JICST-EPlus COPYRIGHT 2003 JST
 AN 910293072 JICST-EPlus
 TI Special issue : the new alchemy.Solvent **extracting** technology.The application to industrial waste.
 AU NISHIMURA SANJI
 CS Kansai Univ., Faculty of Engineering
 SO Kinzoku (Metals & Technology), (1991) vol. 61, no. 1, pp. 30-36. Journal Code: F0157A (Fig. 6, Ref. 19)
 CODEN: KNZKAI; ISSN: 0368-6337
 CY Japan
 DT Journal; Commentary
 LA Japanese
 STA New
 CC SC05060V; WD02030A; XD02030B; UA07090M (628.477; 669.2/.8.05; 66.061.3; 622.775/.776)
 CT solvent **extraction**; scrap; resource **recovery**; metallurgical slime; fly ash; roasting(mineral dressing); liquid-liquid **extraction**; **extraction** solvent; superalloy; nickel base alloy; cobalt containing alloy; electrowinning; zinc; scum; aluminum; amine; **etching solution**; **copper**; waste water treatment; rayon; hydrometallurgy; **recovery** of useful material; sintered ores; pyrites
 BT **extraction**; separation; object; recovery; ash; combustion product; product material; beneficiation of ore; heat treatment; treatment; heat resistant alloy; alloy; metallic material; nonferrous alloy; containing alloy; sampling and winning; smelting; manufacturing; 2B group element; transition metal; metallic element; element; fourth row element; 3B group element; third row element; 1B group element; sewage treatment;

water and sewage treatment; man-made fiber; fiber; cellulosic fiber; ore; iron ore; metal ores

L20 ANSWER 30 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1991(3):42-238 METADEX

TI Anodic Reactions and the Recycling of Metals Utilizing Electrolysis.

AU Wiaux, J.P.; Nguyen, T.

CS Titallyse

SO Metal Finishing (Nov. 1990) 88, (11), 49-55

ISSN: 0026-0576

DT Journal

LA English

AB The anodic reactions which accompany the electrolysis of heavy metals in industrial effluents prove to be complementary to the cathodic reactions. In a number of applications the anodic process can become the principal objective in the treatment of industrial effluents. Some examples are: the simple oxidation of OH⁻ ions to regenerate the acidity in an etch bath, the destruction of inorganic anionic species such as cyanides, the degradation of components present in electroplating baths. The examples cited have been developed and applied on an industrial scale. The electrochemical oxidation process combined with the heavy metal recovery on the cathode can be a reliable economic technique for the complete treatment of industrial effluents. Graphs. 4 ref.-J.H.

CC 42 EXTRACTION AND SMELTING

CT Plating bath wastes: Recovering; Copper: Extraction; Electrolysis; Pollution abatement; Water purification

ET H⁺O; OH; OH⁻; O cp; cp; H cp; OH in 1; in 1

L20 ANSWER 31 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1992(8):42-689 METADEX

TI Extraction of Copper With Kelex-100 From Hydrochloric Acid Etching Solutions.

AU Kyuchukov, G. (Bulgarian Academy of Sciences); Kunev, R. (Bulgarian Academy of Sciences)

SO Khimiya i Industriya (1990) 61, (5-6), 24-26, Graphs, 7 ref.

ISSN: 0368-5764

DT Journal

CY Bulgaria

LA Bulgarian

AB A study of the extraction of Cu from acidic solutions by a mixture of the amine reagent, Kelex-100 (20%), octanol (15%) and kerosene (65%) is presented. A procedure for the recovery of Cu from etching solutions is proposed and the optimum conditions are indicated. The procedure involved washing the Cu-laden extractant with aqueous ammonia, to remove the chloride ions, and the subsequent recovery of the Cu electrolytically, after acidifying with 5.77N H₂SO₄. The extractant was regenerated with 4.1M ammonium chloride.

CC 42 Extraction and Smelting

CT Journal Article; Copper: Extraction; Extraction; Recovering; Washing; Acidification

ET Cu; N; H⁺O*S; H₂SO₄; H cp; cp; S cp; O cp

L20 ANSWER 32 OF 57 JICST-EPlus COPYRIGHT 2003 JST

AN 910787735 JICST-EPlus

TI Recovery of valuables from industrial waste by solvent **extraction**

AU NISHIMURA SANJI; SHIBATA JUNJI

CS Kansai Univ., Faculty of Engineering

SO Shigen, Sozai, (1990) vol. 1990, no. U, pp. 13-16. Journal Code: S0387B (Ref. 24)

CY Japan
DT Conference; Short Communication
LA Japanese
STA New
CC SC05060V; XD02030B (628.477; 66.061.3)
CT solvent **extraction**; **recovery** of useful material; waste treatment; resource recycling; scrap; sludge treatment; fly ash; slag; waste water treatment; industrial waste water; nickel base alloy; cobalt containing alloy; chloride; organic solvent; electrowinning; samarium base alloy; aluminum; titanium oxide; iron oxide; battery; **etching solution**; **copper**; rayon; zinc
BT **extraction**; separation; resource recovery; recovery; treatment; regeneration; object; ash; combustion product; product material; sewage treatment; water and sewage treatment; industrial waste; waste; waste water; liquid waste; sewage; nonferrous alloy; alloy; metallic material; containing alloy; chlorine compound; halogen compound; halide; solvent; component; sampling and winning; smelting; manufacturing; rare earth base alloy; metallic element; element; 3B group element; third row element; metal oxide; oxide; chalcogenide; oxygen group element compound; oxygen compound; titanium compound; 4A group element compound; transition metal compound; iron compound; iron group element compound; 1B group element; transition metal; fourth row element; man-made fiber; fiber; cellulosic fiber; 2B group element
L20 ANSWER 33 OF 57 METADEX COPYRIGHT 2003 CSA
AN 1990(7):43-155 METADEX
TI Method for the Recovery of Metals From Chloride Solutions.
AU Kyuchoukov, G.D.; Mihaylov, I.O.; Elenkov, D.G.; Boyadjiev, L.A.; Fletcher, A.W.
CS Institut po Injenerna Chemia
PI EP 301783 1 Feb. 1989
AD 25 July 1988
DT Patent
LA English
AB A method for the recovery of metals, generally heavy metals or chelatable metals such as Zn or Cu from chloride solutions such as acid chloride etching solutions comprises extracting the metal with a mixed extracting agent of anion exchange/chelating, solvating/cation exchange or anion exchange/cation exchange character, separating the organic phase, washing it with water, aqueous ammonia or aqueous ammoniacal ammonium sulphate, stripping the metal from the organic phase thereby obtained by contacting it with sulphuric acid and returning the organic phase to the extraction stage for reuse after regenerating it.
CC 43 REFINING AND PURIFICATION
CT Zinc: Recovering; Copper: Recovering; Hydrochloric acid; Etchants; Recovering; Chelating; Ion exchanging; Patents
ET Zn; Cu
L20 ANSWER 34 OF 57 HCAPLUS COPYRIGHT 2003 ACS
AN 1990:561170 HCAPLUS
DN 113:161170
TI Anode reactions and metals recycling by electrolysis: complementary processes in waste management
AU Wiaux, J. P.; Nguyen, T.
CS Titallyse S. A., Meyrin/Geneva, CH-1217, Switz.
SO Proceedings of the AESF Annual Technical Conference (1989), 76th, J3, 7 pp.
CODEN: PATCEY; ISSN: 1075-7988
DT Journal
LA English

- CC 72-8 (Electrochemistry)
Section cross-reference(s): 60, 76
- AB Using the RETEC electrolytic cell in wastewater treatment, **electroplating** of 18 karat Au-Cu-Cd alloy with simultaneous electrochem. destruction of the CN- with and without NaCl addn. is discussed. Electrolysis of a spent Cu etch both from etching of Cu in the printed circuit board industry with H2O2 and H2SO4 results in Cu electrorecovery and electrochem. destruction of H2O2. Cu is electrorecovered from an electroless **plating** bath contg. quadrol and this **complexing** agent is oxidized at the anode.
- ST electrolytic cell wastewater treatment; **copper** electrorecovery wastewater; cyanide electrochem destruction wastewater; quadrol electrochem oxidn **copper recovery**; gold **copper** cadmium **electroplating**; **etching** spent bath **copper** electrorecovery; printed circuit etching **copper** electrorecovery; hydrogen peroxide destruction **copper** electrorecovery; complementary process electrochem treatment wastewater
- IT Electrolytic cells
(for wastewater treatment, with complementary processes)
- IT Etching
(of copper by hydrogen sulfide-sulfuric acid etchant, electrochem. treatment of wastewater from)
- IT Electrodeposition and **Electroplating**
(wastewater electrochem. treatment in, complementary processes in)
- IT Wastewater treatment
(electrochem., complementary processes in)
- IT Coating process
(electroless, electrochem. treatment of wastewater from)
- IT Wastewater treatment
(oxidn., electrochem., complementary processes in)
- IT 39471-71-1
RL: PRP (Properties)
(**electroplating** of, from wastewater, with electrochem. destruction of cyanide with and without sodium chloride additive)
- IT 7647-14-5, Sodium chloride, uses and miscellaneous
RL: USES (Uses)
(in electrochem. destruction of cyanide with gold-copper-cadmium alloy **electroplating**)
- IT 102-60-3, Quadrol
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidn. of, electrochem., from wastewater from electroless **plating** of copper)
- IT 57-12-5, Cyanide, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidn. of, electrochem., in gold-copper-cadmium alloy **electroplating**)
- IT 7440-50-8P, Copper, preparation
RL: PREP (Preparation)
(**recovery** of, electrochem., from wastewater from etching or electroless **plating**)
- IT 7722-84-1, Hydrogen peroxide, uses and miscellaneous
RL: REM (Removal or disposal); PROC (Process)
(removal of, electrochem., in electrorecovery of copper from spent **etching bath**)
- L20 ANSWER 35 OF 57 WPIX (C) 2003 THOMSON DERWENT
AN 1988-312920 [44] WPIX
DNN N1988-237283 DNC C1988-138591
TI Spent **etching soln.** regenerator - has modules for selective metal **extn.** oxidn. and hyperfiltration.

DC" M14 X25
IN ALEKBEROVA, V V; DULINA, M Y U; KRAVETS, V V
PA (KIFO) KIEV FOOD IND TECHN INST
CYC 1
PI SU 1388460 A 19880415 (198844)* 4p
ADT SU 1388460 A SU 1986-4127754 19861003
PRAI SU 1986-4127754 19861003
IC C23F001-46
AB SU 1388460 A UPAB: 19930923

The **recovery** of valuable components from the spent **etching soln.** and from water is ensured with the module for selective **extn.** of metal which features an average vessel, ion exchange filters, filtrate regenerated soln. and eluate collectors. The oxidn. module comprises a reactor, metering pumps, reagents holders and a control loop of filtrate quality based on a transducer of optical density which is fitted in the outlet pipe in front of ion-exchange filter and a computer.

The spent **soln.** from the **etching bath** (1) enters the averager tank (3) where the pH level is adjusted by feeding the wash water from the bath (2) and by stirring. The treating soln. is then transferred to the ion exchange filter (5) by pump (4) and via the control valve (31) to ensure the **extn.** of **Cu**. This is followed by feeding the treated soln. to the oxidising reactor (15) while the valve (32) divides the stream into two flows. The greater part of the stream is diverted to the reactor, while the small part passes through the transducer (6) of optical density to check the quality of the filtrate. The concn. control module operates with hyperfiltration.

ADVANTAGE - The unit ensures the regeneration of **etching soln.** based on ferric chloride and re-uses **copper**.
Bul.14/15.4.88.

1/1

FS CPI EPI
FA AB; GI
MC CPI: M14-A03
EPI: X25-R06

L20 ANSWER 36 OF 57 JICST-EPlus COPYRIGHT 2003 JST
AN 890120825 JICST-EPlus
TI Ammonia alkaline etchant recycling.
AU TUKADA NORIAKI
CS Yamatoyashokai
SO Jitsumu Hyomen Gijutsu, (1988) vol. 35, no. 11, pp. 573-577. Journal Code: G0518A (Fig. 6)
CODEN: JHGJA3; ISSN: 0368-2358
CY Japan
DT Journal; Commentary
LA Japanese
STA New
CC NA050400 (621.3.049.75)
CT printed board; **etching solution**; waste water treatment; **copper**; **recovery** of useful material; regeneration; recirculation; ammonium chloride; ammonium hydroxide; mixed liquid; **copper complex**; ammine **complex**; chloride; solvent **extraction**; **extraction** liquid; stripping; electrowinning; flow chart; processing equipment
BT substrate(plate); plate classified by application; plate(material); electric apparatus and parts; parts; sewage treatment; water and sewage treatment; treatment; 1B group element; transition metal; metallic element; element; fourth row element; resource **recovery**; **recovery**; circulation; ammonium compound; onium compound; hydrogen

compound; nitrogen compound; nitrogen group element compound; chlorine compound; halogen compound; halide; hydroxide; oxygen compound; oxygen group element compound; liquid; mixture; object; 1B group element **complex**; transition metal **complex**; metal **complex** ; **complex**(compound); coordination compound; compound(chemical); transition metal compound; 1B group element compound; **copper** compound; **extraction**; separation; sampling and winning; smelting; manufacturing; drawing(diagram); diagram and table; equipment

L20 ANSWER 37 OF 57 HCAPLUS COPYRIGHT 2003 ACS

AN 1988:416260 HCAPLUS

DN 109:16260

TI Monitoring the copper-diketone [**complex**] concentration when recycling copper from etchants

AU Law, H. H.; Tierney, V.; Smith, C. G.

CS AT and T Bell Lab., Murray Hill, NJ, 07974, USA

SO Plating and Surface Finishing (1988), 75(4), 67-9

CODEN: PSFMDH; ISSN: 0360-3164

DT Journal

LA English

CC 79-6 (Inorganic Analytical Chemistry)

Section cross-reference(s): 76

AB Ph alkyl beta-diketone is an effective **complexing** agent for

copper recovery from ammoniacal leaches of

copper-bearing scrap and spent etchants in printed circuit board

manufg. It makes possible the direct transfer of cupric ions to

plating baths. Successful implementation eliminates the need for

copper anodes and reduces the amt. of spent etchant generated. A

technique that uses a trifurcated, fiber-optic sensor was identified for

detg. the **copper**-diketone **complex** concn. With this

technique, the error is <5% and the preferred **copper** concn. is

0.1-20 g/L. The logarithmic ratio of absorbances at 720 and 850 nm is

proportional to concn.

ST copper diketone **complex** detn etchant; etchant analysis copper

diketone **complex**; spectrophotometry copper diketone

complex detn; optical fiber spectrometer etchant analysis

IT Etching

(**copper recovery** from solns. in,

monitoring **copper**-diketone **complexes** in relation

to)

IT Spectrometers

(with optical fibers, for monitoring copper-diketone **complexes**

)

IT Ketones, compounds

RL: ANT (Analyte); ANST (Analytical study)

(1,3-di-, copper **complexes**, detn. of, during recycling copper

from etchants)

IT 7440-50-8DP, Copper, **complexes** with Ph alkyl

beta-diketone

RL: ANT (Analyte); ANST (Analytical study); **PREP (Preparation)**

(detn. of, during **recovery** from solns. in printed circuit

board manufg., spectrometer with optical fibers for)

IT 7440-50-8P, Copper, preparation

RL: **PREP (Preparation)**

(**recovery** of, from solns. in printed circuit board manufg.,

ketone **complex** monitoring in)

L20 ANSWER 38 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1988(5):42-820 METADEX

TI Recovery of Etching Solutions in Printed Circuit Board Manufacturing

Plants.

AU Blinov, S.M.; Ocheretenko, V.A.
SO Prib. Sist. Upr. (1987) (9), 38
ISSN: 0032-8154
DT Journal
LA Russian
AB Three types of recovery installations for Fe-copper chloride and copper ammonium etching solution recovery were built and tested. The main characteristics such as productivity, Cu removed by etching, power, overall size, and mass, of these installations are shown. The purity of recovered Cu is indicated as are future uses of Cu from each installation. Annual savings of 30 000 rubles/installation are reported. 2 ref.-J.G.

CC 42 EXTRACTION AND SMELTING
CT Copper: Extraction; Recovering; Decomposition reactions; Precipitators: Development; Economics
ET Fe; Cu

L20 ANSWER 39 OF 57 WPIX (C) 2003 THOMSON DERWENT
AN 1985-271131 [44] WPIX
DNC C1985-117517
TI Organogel for **recovery** of ammoniacal **copper** - comprises hydrophobic polymer contg. **copper** ion-exchange agent.

DC A35 L03 M25
IN BABCOCK, W C; BAKER, R W; BROOKE, J W; TUTTLE, M E
PA (BEND-N) BEND RES INC
CYC 14
PI EP 159450 A 19851030 (198544)* EN 30p
R: AT BE CH DE FR GB IT LI LU NL SE
JP 60209262 A 19851021 (198548)
US 4622344 A 19861111 (198648)
EP 159450 B 19890308 (198910) EN
R: AT BE CH DE FR GB IT LI LU NL SE
DE 3476971 G 19890413 (198916)
CA 1269491 A 19900522 (199027)

ADT EP 159450 A EP 1984-309084 19841227; US 4622344 A US 1984-585977 19840305
PRAI US 1984-585977 19840305
REP 1.Jnl.Ref; DE 2451006; EP 101943; FR 2120753; FR 2256112; GB 1499797; GB 894392; US 4220726; US 4305912
IC B01J039-20; B01J045-00; B01J047-00; C01G003-00; C08D005-20; C22C003-00; **C23F001-00**

AB EP 159450 A UPAB: 19930925
A gel for use as a **Cu** ion-exchange medium comprises a hydrophobic nonporous polymer plasticised and swollen with a monomeric organic liquid **Cu** ion-exchange agent (I). Pref. the polymer has been polymerised in the presence of (I) and is plasticised and swollen in presence of an organic solvent.

Recovery of cupric ion from a cupric ion-contg. ammoniacal soln. comprises contacting the soln. with the gel medium and stripping cupric ion from the medium by contacting the latter with an acid soln. Also claimed is 1-n-octylphenyl -p-1,3-butanedione (II).

USE/ADVANTAGE - The process is claimed for the **recovery** and regeneration of spent ammoniacal printed circuit board etchant by contact the spent **etchant soln.** with (I). The process does not involve extensive liquid-liquid separations. The ion-exchange medium has superior agent (I) retention, a long life and is reusable.

0/0
FS CPI
FA AB
MC CPI: A12-M; A12-S; A12-W11F; L03-H04E; M14-A; M25-E

L20 ANSWER 40 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1984-232043 [38] WPIX

DNN N1984-173517 DNC C1984-097959

TI Combined **etching soln.** regeneration and metal recovery
- from basic and acidic solns. by liq.-liq. **extraction.**

DC L03 M14 V04

IN BENDER, H; BOHM, A; REINARTZ, D

PA (DIDI) DIDIER-WERKE AG

CYC 5

PI DE 3308849 A 19840913 (198438)* 11p

FR 2542325 A 19840914 (198442)

NL 8400768 A 19841001 (198444)

AT 8400824 A 19860415 (198620)

DE 3308849 C 19870730 (198730)

IT 1199074 B 19881230 (199116)

ADT DE 3308849 A DE 1983-3308849 19830312; FR 2542325 A FR 1984-3678 19840309;
NL 8400768 A NL 1984-768 19840309

PRAI DE 1983-3308849 19830312

IC B01D011-04; C22B007-00; C22B015-00; **C23F001-00;**
C23F017-00; C23G001-36; C25C001-00; **C25F007-02;**
H05K003-06

AB DE 3308849 A UPAB: 19930925

Treatment of metal (esp. **copper**) contg. basic and acidic
etching solns. comprises (i) treating a basic
etching soln. with a liq. **extractant** to
extract metal; (ii) sepg. the **extractant** from the soln.;
(iii) contacting the **extractant** with an acidic **etching**
soln.; (iv) sepg. the **soln.** from the **extractant**
; and (v) **recovering** metal by electrolysis.USE/ADVANTAGE - Useful for treating used **etching**
solns. from **etching** of printed circuit boards and allows
efficient regeneration of at least the basic **etching**
soln. and metal **recovery**, in the metallic form, from
both acidic and basic **etching solns.** at a central
site. Process residues cause no environmental pollution.
0/1

FS CPI EPI

FA AB

MC CPI: L03-D03C; L03-H04E; M14-A; M25-G08

EPI: V04-R09

L20 ANSWER 41 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1984-208150 [34] WPIX

DNN N1984-155627 DNC C1984-087507

TI Electrolyte regeneration of ammoniacal **etching soln.** -
used for **etching** of copper.

DC L03 M14 V04

IN HAAS, R; HOLLMULLER, H; KONSTANTOU, E; HOELLMUELLER, H; KONSTANTOUROS, E

PA (SIEI) SIEMENS AG

CYC 1

PI DE 3305319 A 19840816 (198434)* 14p

DE 3348401 A 19911010 (199142)

DE 3305319 C2 19930121 (199303) 6p C23F001-46 <--

DE 3348401 C2 19930826 (199334) 5p C23F001-18 <--

ADT DE 3305319 A DE 1983-3305319 19830216; DE 3348401 A DE 1983-3348401
19830216; DE 3305319 C2 DE 1983-3305319 19830216; DE 3348401 C2 Div ex DE
1983-3305319 19830216, DE 1983-3348401 19830216

FDT DE 3305319 C2 Div in DE 3348401; DE 3348401 C2 Div ex DE 3305319

PRAI DE 1983-3305319 19830216; DE 1983-3348401 19830216

IC ICM **C23F001-18; C23F001-46**

ICS C25D003-38; C25F007-02

AB DE 3305319 A UPAB: 19930925

In an electrolytic, complete regeneration process for ammoniacal **etching soln.**, the **etching soln.** contains tetrammine cupric sulphate, ammonia and ammonium sulphate and has its etching rate increased by means of a catalyst, and dissolved **copper** and used etching chemicals are continuously **recovered** in the etching circuit by direct electrolysis of the **etching soln.**

USE/ADVANTAGE - The process is used esp. for regeneration of **etching solns.** used in **etching** of circuit boards as well as chemically machined **copper** (alloy) parts. **Copper** is **recovered** without employing liq.-liq. **extraction** and the **etching** rate of the **soln.** is increased without active carbon addn.

1/2

FS CPI EPI

FA AB; GI

MC CPI: L03-D03C; M14-A

EPI: V04-R01; V04-R09

L20 ANSWER 42 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1983(5):58-507 METADEX

TI Disposal of Critical Process Solutions in Relation to Material Recovery.

AU Dengler, H.

SO Metalloberflache (Sept. 1982) 36, (9), 425-428

ISSN: 0026-0797

DT Journal

LA German

AB The treatment and recovery of materials from etching solutions, chemical Cu baths and ion-exchange regenerates is described. Ammonical etch baths, persulphate etches, and the need for the separation of process solution contg. complexants are considered. Electrodeposition and chemical precipitation methods, and the treatment of low vols. are discussed.-H.S.

CC 58 METALLIC COATING

CT Etching; Plating baths; Ion exchanging; Wastes; Recovering; Materials conservation

ET Cu

L20 ANSWER 43 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1981(12):63-669 METADEX

TI Circuit Boards by a New Method: Both Etch Bath and Copper Are Re-used.

AU Sandstrom, L.

SO Ny Tek. (29 May 1981) (22), 16

DT Journal

LA Swedish

AB In normal circuit-board manufacture, the etch bath (a water/ammonia solution) is discarded when saturated with Cu. A Swedish firm, backed by various organisations, has now developed a liquid-extraction method for recovery and re-use of both the liquid and the metal. The saturated liquid is treated with a paraffin solution containing an organic substance which combines with the metal to be extracted. The paraffin solution is then treated with H₂SO₄ before passing to an electrolysis chamber where pure Cu is precipitated on Ti. Etch bath, acid, and metal can then be re-used. The washing water is treated in the same way. The only discharge is pure water.-R.J.F.

CC 63 ELECTRONIC DEVICES

CT Printed circuits; Copper: Recovering; Recycling; Etchants: Recovering

ET Re; Cu; H⁺O⁺S; H₂SO₄; H cp; cp; S cp; O cp; Ti

L20 ANSWER 44 OF 57 JAPIO COPYRIGHT 2003 JPO
AN 1980-145177 JAPIO
TI TREATING METHOD OF ALKALI **ETCHANT** WASTE SOLUTION
IN IKEDA SABURO; NAKANO YOSHIO; HONDA KAZUhide
PA KAGAKU GIJUTSU SHINKOUKAI
PI JP 55145177 A 19801112 Showa
AI JP 1979-52741 (JP54052741 Showa) 19790428
PRAI JP 1979-52741 19790428
SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1980
IC ICM C23F001-00
ICS C02F001-26
AB PURPOSE: To regenerate alkali **etchant** waste soln. and to **recover copper** simultaneously thereby treating waste soln. effectively, by treating alkali **etchant** waste soln. with naphthenic acid to remove **copper**.
CONSTITUTION: Raw soln. sent from an alkali **etchant** waste soln. tank 1 is mixed in a primary **extraction** tank 2 with naphthenic acid for removing **copper** sent from a secondary reverse **extraction** and settling tank R<SB>2</SB>, then it is delivered to a primary **extraction** and settling tank T<SB>1</SB>. Regenerated soln. separated in the tank T<SB>1</SB> is mixed in a secondary **extraction** tank 3 with **copper**-removing naphthenic acid sent from a reverse **extraction** and settling tank R<SB>1</SB> and is delivered to a secondary **extraction** and settling tank T<SB>2</SB>. The final regenerated soln. separated in the tank T<SB>2</SB> is delivered through a solvent-separating cylinder 9 to a regenerated **etchant** tank 4. Dil. sulfuric acid sent from a sulfuric acid tank 5 is delivered to a reverse **extraction** tank 6, where it is mixed with **copper** naphthenate, then separated from the naphthenic acid in the reverse **extraction** tank R<SB>1</SB> to form sulfuric acid soln. contg. **copper** sulphate, which is mixed in a reverse **extraction** tank 7 with **copper** naphthenate then **copper** is reversely **extracted** from the soln. in the reverse **extraction** and settling tank R<SB>2</SB>. These procedures permits to produce regenerated soln. which is similar to a fresh **etchant**.
COPYRIGHT: (C)1980, JPO&Japio

L20 ANSWER 45 OF 57 JAPIO COPYRIGHT 2003 JPO
AN 1980-091979 JAPIO
TI RECOVERING AND CIRCULATING APPARATUS FOR ALKALINE **ETCHING** WASTE SOLUTION
IN TSUKADA NORIAKI; OKAMOTO KUNIO
PA YAMATOYA SHOKAI:KK
PI JP 55091979 A 19800711 Showa
AI JP 1978-162839 (JP53162839 Showa) 19781229
PRAI JP 1978-162839 19781229
SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1980
IC ICM C23F001-08
AB PURPOSE: To enable NH<SB>3</SB> and chlorine ion to be recycled by combinedly setting a unit for separating an **etching** waste soln. into a **copper**-contg. oil layer and a water layer with a **copper** **extracting** reagent, a unit for treating the oil layer with sulfuric acid, a unit for treating the water layer with a **recovering** soln., etc. through control mechanisms.
CONSTITUTION: An alkali **etching** waste soln. contg. Cu(NH<SB>3</SB>)<SB>3</SB>Cl, etc. is introduced into **copper** **extraction** container 12 through auxiliary container 3 and waste soln. container 8. In container 12 a **copper** **extracting** reagent is added to the soln. from container 14 and

agitated to separate the soln. into an oil layer ($R\langle SB\rangle_2\langle SB\rangle Cu$) and a water layer [$Cu(NH\langle SB\rangle_3\langle SB\rangle)\langle SB\rangle_2\langle SB\rangle Cl$] through separation plate 63. The water layer is introduced into container 26 through oil adsorption column 25, pH-adjusted, and treated with a **recovering** soln. ($NH\langle SB\rangle_3\langle SB\rangle$ soln. + ammonium chliride) from container 29 to regenerate $NH\langle SB\rangle_3\langle SB\rangle$ and chlorine ion according to the reaction equation. They are fed to container 34 and recycled to etching machine 1. On the other hand, the oil layer is treated with sulfuric acid in back **extraction** container 41 to be separated into RH and **copper** sulfate. **Copper** is **recovered** from the **copper** sulfate, and the RH is reused as the **copper** **extracting** reagent through containers 48, 14. The above- mentioned operations are automatically controlled with control box 5 through pumps, level gauges, pH meters, etc.
 COPYRIGHT: (C)1980,JPO&Japio

L20 ANSWER 46 OF 57 METADEX COPYRIGHT 2003 CSA

AN 1981(6):57-316 METADEX

TI Basics and Potential Applications of Electrochemical Recycling.

AU Fabjan, Ch.

SO Oberflache Surf. (Dec. 1980) 21, (12), 283-292

DT Journal

LA German

AB Systems for regeneration of Cu etching baths are described. Fixed bed particle electrodes consisting of conductive particles of defined grain size (e.g. graphite grains 1-1.5 mm in dia.) in contact with each other are described for compact, short processing time installations. Oxidative regeneration of chromic acid etching solutions for plastic plating is described. Regeneration is performed in diaphragm cells with Pb alloy electrodes. A process is detailed for producing circuit boards in which the electrolyte contains a 25% suspension of graphite and in which etching and regeneration occur simultaneously. Purification of complex metal cyanide solutions by ozone treatment, precipitation of metal ions by use of reductants such as hydrogen, formaldehyde or formic acid in the presence of electrochemically active catalysts and electrodialysis of salt solutions for water purification are also described. 21 refs.-B.L.

CC 57 FINISHING

CT Etchants: Recovering; Recycling; Pollution abatement; Printed circuits: Coating

ET Cu; Pb

L20 ANSWER 47 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1979-84601B [47] WPIX

TI Regeneration of ammoniacal **etching** soln. by liq.-liq. **extn.** of copper - in a process which also **extracts** copper from washing water.

DC E35 L03 M14 P43

IN OTTERTUN, H D; REINHARDT, H

PA (MXPR-N) MX PROCESSER REINH

CYC 9

PI EP 5415 A 19791114 (197947)* EN

R: CH DE FR GB IT NL

SE 7805037 A 19791203 (197951)

JP 54146233 A 19791115 (198001)

US 4252621 A 19810224 (198111)

EP 5415 B 19820217 (198208) EN

R: CH DE FR GB IT NL

DE 2962121 G 19820325 (198213)

JP 62053592 B 19871111 (198748)

PRAI SE 1978-5037 19780502

REP AU 469403; US 3440036; US 4058585; 1.Jnl.Ref
 IC B08B007-04; C01G003-00; C22B015-12; **C23F001-00**; C23G001-36;
 C25C001-12; **C25F001-00**; **C25F007-02**
 AB EP 5415 A UPAB: 19930901

A spent ammoniacal **soln.** resulting from **etching** Cu objects and contg. free ammonia, ≥ 1 ammonium salt and, opt. an oxidising agent is regenerated by (a) contacting the **soln.**, together with water used for washing the etched object, in two separate **extn.** steps, with an organic **soln.** contg. an **extractant** for Cu; (b) recycling the **etching soln.**; (c) contacting the organic **soln.** from the other **extn.** with aq. H₂SO₄ **soln.** to re-**extract** Cu; and (d) recycling the organic **soln.** obtd. in (c) to the **extn.** steps.

The **etching soln.** can be recycled a large number of times. Metallic Cu can be **recovered** in high purity from both **etching** and washing **solns.** (allowing the latter to be discarded in a municipal sewer) Cu ions are selectively **extracted** and not chloride ions, so no extra stripping operation is required. Process is esp. suitable for **recovering** Cu from printed circuit etching effluent.

FS CPI GMPI

FA AB

MC CPI: E31-F05; E32-A; E35-A; L03-H04E; M14-A

L20 ANSWER 48 OF 57 METADEX COPYRIGHT 2003 CSA DUPLICATE 6
 AN 1980(11):58-880 METADEX
 TI Dealing with Critical Process Solutions in Relation to the Recovery of Materials.

AU Dengler, H.

SO Galvanotechnik (July 1979) 70, (7), 604-609

DT Journal

LA German

AB The treatment of used etching baths, chemical copper plating baths, and ion exchange eluates require a knowledge of the possible processes and the prevailing operating parameters in order to select the most suitable method of treatment. Solutions which are free from complex-formers and those which contain them are dealt with separately. Taking as examples the treatment of etching solutions based on ammonia, ammonium persulphate or cuprous chloride, of EDTA-containing copper solutions, as well as of ion exchange eluates, the possibilities for the processing of spent operating solutions and also the recovery of the materials they contain are described.-AA

CC 58 METALLIC COATING

CT Effluents; Copper: Recovering; Plating baths; Etching; Ion exchanging; Recovering

L20 ANSWER 49 OF 57 WPIX (C) 2003 THOMSON DERWENT
 AN 1976-15396X [09] WPIX
 TI **Etching solution** for printed circuits - contg. hydrogen peroxide and inorganic acids for easy **copper recovery**.

DC M14 U11 U12 V04

PA (HITA) HITACHI LTD

CYC 1

PI JP 51002975 A 19760112 (197609)*

PRAI JP 1974-73336 19740628

IC **C23F001-00**; H01L021-28; **H05K003-00**

AB JP 51002975 A UPAB: 19930901

Etching soln. for printed circuits mfg. capable of being easily treated for metal **recovery** after etching operation,

contains hydrochloric acid, an inorganic acid, sulphuric, nitric, phosphoric and boric acids or their salts e.g. sodium nitrate, and a hydrogen peroxide soln. Heavy metals except **copper** and **copper-complex-forming** material are not present in waste water after printed circuit **etching** by this **etching soln.**

FS CPI EPI

FA AB

MC CPI: M14-A

L20 ANSWER 50 OF 57 HCAPLUS COPYRIGHT 2003 ACS DUPLICATE 7

AN 1974:415988 HCAPLUS

DN 81:15988

TI Processing of spent copper **etching solutions** for electroless copper **plating**

IN Ruff, Claus W.

PA Loewe Opta G.m.b.H

SO Ger. Offen., 8 pp.

CODEN: GWXXBX

DT Patent

LA German

IC C23C; C23F

CC 56-5 (Nonferrous Metals and Alloys)

Section cross-reference(s): 60, 71

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 2244307	A1	19740328	DE 1972-2244307	19720909
	DE 2244307	B2	19750821		
	SE 387966	B	19760920	SE 1973-9677	19730710
	CH 606470	A	19781031	CH 1973-10232	19730713
	AT 324065	B	19750811	AT 1973-7006	19730809
	US 3855141	A	19741217	US 1973-390553	19730822
	GB 1416637	A	19751203	GB 1973-41712	19730905
	FR 2199009	A1	19740405	FR 1973-32189	19730906
	IT 993886	A	19750930	IT 1973-28632	19730906
	JP 50110948	A2	19750901	JP 1973-100400	19730907
	JP 55049155	B4	19801210		
PRAI	DE 1972-2244307		19720909		

AB Spent CuCl₂ baths from the etching of Cu were processed for the electroless autocatalytic Cu **plating** in the manuf. of conductive patterns by enrichment to a const. metal content, adding an oxidizing agent, e.g. chlorate, in excess for oxidn. of Cu(I), and subsequently an alk. **complexing** agent, e.g. EDTA, of pH 11.5-12.5.

ST **copper plating bath; electroless copper plating bath recovery; conductive pattern bath; etching copper bath processing**

IT **Etching**
(of copper, bath recovery for copper electric plating with)

IT Electric circuits
(printed, copper in spent **etching soln.** for)

IT Coating process
(with copper, from spent **etching bath**)

IT 7440-50-8, uses and miscellaneous
RL: USES (Uses)
(coating with, from spent **etching bath**)

L20 ANSWER 51 OF 57 WPIX (C) 2003 THOMSON DERWENT

AN 1974-19639V [11] WPIX

TI* Cupric chloride-contg **etching soln** regeneration - by oxidising cuprous chloride and recovery of hydrogen chloride and oxygen using part of cupric chloride.

DC A91 M14

PA (BACH-N) BACH & CO

CYC 1

PI DE 2241462 A 19740307 (197411)*

PRAI DE 1972-2241462 19720823

IC C23F001-00

AB DE 2241462 A UPAB: 19930831

Recovery of HCl and O₂ in process for regenerating CuCl₂-contg. **etching soln.** by removing CuCl soln. formed from **etching** compartment, oxidising CuCl with HCl and O₂ and recycling half of regenerated CuCl₂ soln. to **etching** compartment, is effected by (a) charging the other half of regenerated CuCl₂ soln. to a cation exchanger and **extracting Cu** with formation of HCl, according to equation : $\text{CuCl}_2 + \text{H}_2\text{X} \rightarrow \text{CuX} + 2 \text{HCl}$, (where X is a divalent organic gp.); (b) recycling HCl to regenerating chamber; (c) reacting CuX formed with H₂SO₄ to form H₂X, re - usable for **Cu extn.**, and CuSO₄, according to equation : $\text{CuX} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{X} + \text{CuSO}_4$; (d) passing CuSO₄ soln. formed to an electrolysis compartment and decomposing it to **Cu**, H₂SO₄ and O₂ according to equation : $\text{CuSO}_4 + \text{H}_2\text{O} + \text{energy} \rightarrow \text{Cu} + \text{H}_2\text{SO}_4 + 1/2 \text{O}_2$ and (e) recycling H₂SO₄ to cation exchanger and O₂ to regenerating chamber. Pref. X is a resin, e.g. an epoxy resin, polystyrene or polyacrylate with -SO₂H or -COOH gps. Process is useful in etching **Cu** or **Cu** alloys, e.g. in prodn. of printed circuits from **Cu**-coated insulators.

FS CPI

FA AB

MC CPI: A12-M; M14-A; M25-G08

L20 ANSWER 52 OF 57 HCAPLUS COPYRIGHT 2003 ACS

AN 1973:60816 HCAPLUS

DN 78:60816

TI Development and testing of an experimental industrial apparatus for **extracting** copper from spent etching baths of **electroplating** shops of the Cheboksary electrical equipment plant.

I

AU Katitskii, D. G.; Skrebkov, G. P.; Ivanov, A. I.; Logunov, G. I.; Budnichenko, V. A.; Matveeva, A. M.

CS USSR

SO Khimiya i Khimicheskaya Tekhnologiya (Cheboksary, USSR) (1970), No. 1, 35-44

CODEN: KKMTAR; ISSN: 0368-5985

DT Journal

LA Russian

CC 54-2 (Extractive Metallurgy)

AB Results of the 1st stage of the title study are presented. It was possible to **ext.** >90% Cu from spent etching baths contg. HNO₃ by cementation with Fe. The concn. of Fe in the outgoing liq. and the output of the app. depend on the duration of reaction which must be <30 min.

ST **copper recovery etching bath**

IT 7440-50-8P, preparation

RL: **PREP (Preparation)**

(pptn. of, from spent etching baths, by cementation with iron)

L20 ANSWER 53 OF 57 HCAPLUS COPYRIGHT 2003 ACS

AN 1970:448371 HCAPLUS

DN 73:48371

- TI Neutralization of spent iron(III) chloride solutions and **extraction** of copper
- AU Sitnik, A. B.; Vdovenko, E. N.
- CS USSR
- SO Poligrafiya (1970), (2), 26
CODEN: PLGFAH; ISSN: 0032-2717
- DT Journal
- LA Russian
- CC 60 (Sewage and Wastes)
- AB Spent **solns.** from **etching copper** printing **plates** with FeCl₃ were treated with Fe to ppt. Cu. The sepd. liq. was neutralized with Ca(OH)₂, oxidized by air, and filtered to **recover** Fe(OH)₃. A sievelike plastic basket contg. Fe filings were lowered into the spent soln. at 40-50.degree. until an inserted steel **plate** did not turn reddish and indicator paper showed pH 6-7 (.apprx.1 hr).
- ST **copper recovery etching solns;**
etching solns copper recovery; iron
chloride **etching solns** regeneration
- IT Etching
(of copper printing **plates**, by iron chloride soln., copper removal and iron hydroxide manuf. from spent soln. from)
- IT Printing
(**plates**, etching of copper, copper removal and iron hydroxide manuf. from spent soln. from)
- IT 7705-08-0P, uses and miscellaneous
RL: **PREP (Preparation);** USES (Uses)
(**copper printing plate etching** by
soln. of, **copper** removal and iron hydroxide manuf.
from spent soln. from)
- IT 1309-33-7P
RL: **IMF (Industrial manufacture); PREP (Preparation)**
(manuf. of, from spent **copper-printing-plate**
etching soln.)
- IT 7440-50-8P, uses and miscellaneous
RL: **PREP (Preparation);** USES (Uses)
(printing **plates**, etching of, **copper** removal and
iron hydroxide manuf. from spent soln. from)
- L20 ANSWER 54 OF 57 HCAPLUS COPYRIGHT 2003 ACS
- AN 1925:325 HCAPLUS
- DN 19:325
- OREF 19:37e-i,38a-d
- TI Some functional derivatives of .alpha.-sulfobutyric acid and the rotatory power of their active components
- AU Backer, H. J.; de Boer, J. H.
- SO Rec. chim. trav. (1924), 43, 420-33
- DT Journal
- LA Unavailable
- CC 10 (Organic Chemistry)
- GI For diagram(s), see printed CA Issue.
- AB In a previous paper (C. A. 18, 2499) it was shown that the active acids EtCH- (SO₃H)CO₂H (I) undergo an inversion of sign of optical rotation by the addn. of 2 equivs. of base. This "inversion" is due to a neutralization of the CO₂H. B. and de B. have prepd. derivs. in which this group is substituted, i. e., anilides and benzimidazole derivs. Aniline sulfobutyrate was boiled 2 hrs. with 5 times its wt. of PhNH₂ and on cooling sepd. aniline butyranilide-.alpha.-sulfonate (II), crystd. from H₂O, then from EtOH, m. 253-6.degree.. II decompd. with Ba(OH)₂ or BaCO₃ and evapd. to eliminate PhNH₂ gave the Ba salt [EtCH(CONHPh)SO₃]₂Ba.3H₂O,

hexagonal **plates** that effloresce in the air, losing 1 mol. H₂O. The Ba salt decompd. with the calcd. amt. of CuSO₄, CoSO₄ and NiSO₄, resp., gave the green **Cu** salt, the red Co salt (7H₂O) and the Ni salt (7H₂O). Two g. of the p-toluidine salt of I heated 2 hrs. with 5 g. p-toluidine at 180.degree. gave p-toluidine butyro-p-toluidide-.alpha.-sulfonate, m. 245-50.degree.. p-Anisidine butyro-p-anisidide-.alpha.-sulfonate, m. 242.degree., and p-phenetidine butyro-p-phenetidide-.alpha.-sulfonate, m. 261-2.degree., were obtained similarly. An emulsion of PhNH₂ + H₂O was satd. with SO₂. On standing aniline acid sulfite sepd. as small needles which in the air lose SO₂, giving neutral aniline sulfite (III), H₂SO₃.2PhNH₂.2H₂O. EtCHBrCO₂Et was heated with an excess of 40% aq. III. After some hrs. 2 layers were formed of which the upper was PhNH₂.HBr. The lower layer was EtCH (NHPh) CO₂Et, m. 26-7.degree., which on sapon. gave EtCH(NHPh)-CO₂H, m.140.degree.. o-C₆H₄(NH₂)₂ sulfobutyrate heated 2 hrs. at 180.degree. loses H₂O and solidifies on cooling. A blue by-product that acts as an indicator with acids and alkalies is formed. The main product benzimidazole-2-propylsulfonic acid (IV), NH.C₆H₄.N:CCH₂EtSO₃H, is **purified** by converting it into the Ba or K salt, boiling with charcoal and is pptd. as a white powder on adding acid. IV with Ba(OH)₂ gives the Ba salt (2H₂O) and this decompd. with CoSO₄ gives the Co salt (5H₂O). 3,4-Diaminotoluene sulfobutyrate heated some hrs. at 180.degree. and **purified** as the K salt gave methylbenzimidazole-2-propylsulfonic acid. In order to resolve the dl-acids a soln. of 11.3 g. EtCH- (NHPh)SO₃H was heated with 15.6 g. strychnine and sepd. 20 g. of the alkaloid salt. In order to sop. the less sol. active component it was recrystd. from H₂O several times. To det. the degree of sepn. the "mother liquor method" (C. A. 18, 2499) was used. The mother liquor of each cryst. was treated with an equimol. amt. of Ba(OH)₂, filtered and **extd.** with CHCl₃ to eliminate traces of strychnine. On evapn. was obtained the Ba salt, of which the optical rotation was detd. Detd. in this way the rotation of the 3rd crystn. was + 9.50 while for the 12th and 13th it was -34.degree. and -34.degree., resp. Constancy in the result indicates the end of the sepn. Strychnine l-butyranilide-.alpha.-sulfonate seps. as needles contg. 1 mol. of H₂O of crystn. This salt treated with Ba(OH)₂, etc., gives l-butyranilide-.alpha.-sulfonic acid, mol. rotation, MD -16.5.degree.; the Ba salt, MD -34.degree.; for the **Cu**, Co and Ni salts MD could only be detd. approximately. d- and l-sulfo. butyric acids were converted into the corresponding d- and l-EtCH(NHPh)SO₃H and appear to be identical with the same products obtained on sepg. the dl-mixt. of the latter. Ten g. benzimidazolesulfonic acid (V) and 13.5 g. strychnine were heated with 500 cc. H₂O. The salt obtained was crystd. as above to sep. the 2 isomers. The K salt of the d-isomer of V has a MD 19.7.degree.; the strychnine salt seps. as small tablets; the Ba salt (2H₂O), MD 34.degree.; the Co salt, (5H₂O), MD 28.degree.. o-C₆H₄(NH₂)₂ d-sulfobutyrate heated as above in the prepn. of IV gave a product contg. 66% of the d-isomer of V. While neutralization of active suffobutyric acid inverts the sign of rotation EtCH- (NHPh)SO₃H (VI) gives nearly the same sign of rotation as the normal salts. This observation supports the supposition that the inversion is due to the neutralization of the CO₂H group. The rotations of the Co and Ni salts of VI and the Co salt of IV in EtOH show anomalous dispersion. The optical data so far obtained for these compds. are summarized in a table.

L20 ANSWER 55 OF 57 JAPIO COPYRIGHT 2003 JPO
AN 2000-017462 JAPIO
TI COPPER ETCHING METHOD AND DEVICE THEREFOR
IN KA KENSHIN
PA KA KENSHIN
PI JP 2000017462 A 20000118 Heisei

AI* JP 1998-189243 (JP10189243 Heisei) 19980703
 PRAI JP 1998-189243 19980703
 SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 2000
 IC ICM C23F001-08
 ICS C23F001-18; H05K003-06
 AB PROBLEM TO BE SOLVED: To reduce the amt. of an **etching soln.** to be used by previously charging the inside of an etching tank with at least one kind of **etching soln.** selected from organic acid such as sulfuric acid and hydrochloric acid, furthermore adding an **etching waste soln.** extracted from the **etching** tank with ozone from the outside, thereafter circulating it through the etching tank and executing **copper** etching reaction.
 SOLUTION: Ozone is produced by electrode reaction or ultraviolet irradiation. This device contains an etching tank 1, a roller set 13 transporting a printed circuit board, a nozzle set 14 spraying an **etching soln.**, an **etching waste soln**
 . housing tank 2, a pumping device 3, a gas liq. mixer 4 and an ozone feeding device 5, the **recovered etching soln**
 . passes through the gas liq. mixer 4, is mixed with ozone and is thereafter reused as an **etching soln.**, and, by the high oxidizing power of ozone, **copper** [1] ions are immediately oxidized into **copper** ions. The gas liq. mixer is formed preferably by a Venturi tube.
 COPYRIGHT: (C)2000,JPO

L20 ANSWER 56 OF 57 NTIS COPYRIGHT 2003 NTIS
 AN 1973(35):04523 NTIS Order Number: PB-214 082/0/XAB
 TI Recovery of Metal Values from Chrome **Etching Solutions**
 . Patent application.
 IN Elges, C. H.; Haskett, P. R.; Bauer, D. J.; Lindstrom, R. E.
 PA Department of the Interior, Washington, D.C. (109950)
 NR PB-214 082/0/XAB; PAT-APPL-292 232, DOCKET/MIN-1959
 6p; Filed 3 Oct 72
 AI US 1972-292232 19721003
 DT Patent
 CY United States
 LA English
 AV Government-owned invention available for licensing. Copy of application available NTIS. Order this product from NTIS by: phone at 1-800-553-NTIS (U.S. customers); (703)605-6000 (other countries); fax at (703)605-6900; and email at orders@ntis.gov. NTIS is located at 5285 Port Royal Road, Springfield, VA, 22161, USA.
 NTIS Prices: PC A02/MF A01
 OS GRA&I7305
 AB Chromium and **copper** can be **recovered**, as oxides, from spent chrome **etching solutions** by means of a process comprising the steps of: Addition of a reducing sugar to reduce Cr(VI) to Cr(III) and to **complex** Cr(III) and **Cu** values in solution; Addition of base to raise the pH, to reduce the **copper** and precipitate it as Cu2O; Separating the precipitated Cu2O; Heating the remaining solution at a temperature of about 50 to 70C to break the Cr(III) **complex**; and, Adjusting the pH to precipitate the chromium as hydrous chromium oxide. (Author)
 CC 90 Government Inventions for Licensing
 CT *Etchants; ***Materials recovery**; *Patent applications; Chromium; **Copper**; Precipitation(Chemistry); Neutralizing; Sugars; Reduction(Chemistry)
 UT PAT-CL-23-145

L20 ANSWER 57 OF 57 WPIX (C) 2003 THOMSON DERWENT
 AN 1973-50831U [36] WPIX
 TI Etching of copper - a continuous process involving regeneration of
 etchant soln.
 DC L03 M14
 PA (SHIL) SHIPLEY CO INC
 CYC 5
 PI DE 2306445 A (197336)*
 FR 2171286 A (197349)
 JP 48096429 A 19731210 (197408)
 GB 1426643 A 19760303 (197610)
 CA 989283 A 19760518 (197623)
 PRAI US 1972-224849 19720209
 IC C23F001-00
 AB DE 2306445 A UPAB: 19930831
 An etching system for **copper** e.g. in printed circuiting etc in
 which a continuously cycling and regenerating **etch soln**
 . is used, makes use of a soln contg initially about 4 oz/gall Cu²⁺ ions
 and also organic amines as **complexing** agents as well as NH₂Cl or
 NH₄Br salts. When the **Cu** content of the etchant has risen to
 14-20 oz/gall extra NH₄Cl or NH₄Br is added such that 1 1/2 oz/gall
 addition causes the pptn. of 1 oz/gall **Cu**. By constant or batch
 wise dosing of the etchant in thus means a regenerated soln. for
 continuous use is obt'd. Valuable dissolved **Cu** is
recovered and pollution due to disposal of spent etchant is
 avoided.
 FS CPI
 FA AB
 MC CPI: L03-H04E3; M14-A